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HAZARDOUS EMISSION CHARACTERIZATION OF UTILITY BOILERS

Chatten Cowherd, Jr., et al

Midwest Research Institute

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July 1975

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HAZARDOUS EMISSION CHARACTERIZATION OF UTILITY BOILERS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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The report gives results of a field sampling program aimed at quantifying potentially hazardous pollutants in the waste streams of a representative coal-fired utility boiler: a 125-MW boiler (fired with pulverized coal and equipped with a mechanical fly ash collector) at TVA's Widows Creek steam electric generating station. The combustion products identified as potentially hazardous air pollutants included 22 trace elements, nitrates, sulfates, polycyclic organic compounds, and polychlorinated biphenyls. The waste streams sampled included pulverized coal, furnace bottom ash, superheater ash, collection ash, and flue gases at the fly ash collector inlet and outlet. Acceptable mass balance was achieved for about half of the elemental pollutants. Trace metal enrichment was measured. Study results include recommended modifications of sample collection and preparation methods: larger and more frequent samples of coal and bulk ash streams are expected to improve sample representativeness; development of methodologies for estimating bulk ash flows will permit internal checks on mass balances; and routine chemical analysis of NBS standard coal and fly ash will improve quality assurance of the analytical methods.

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July 1975

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PREFACE

This document was prepared for EPA/CSL under EPA Contract No. 68-02-1324, Task 27. The work reported herein was conducted in three sections of the Physical Sciences Division of Midwest Research Institute. The Program Coordinator was Dr. L. J. Shannon, Head, Environmental Systems Section. Development of the overall sampling plan and analysis of field and laboratory data were performed in this section by Dr. Chatten Cowherd assisted by Ms. Christine Guenther. The field sampling effort was carried out under the direction of Mr. Paul Constant, Head, Environmental Measurements Section, with Mr. William Maxwell serving as crew chief at the test site. The chemical analysis of collected samples was directed by Dr. James Spigarelli, Head, Analytical Chemistry Section, with assistance from Dr. Mark Marcus.

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Physical Sciences Division

July 1975

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SUMMARY

This report presents the results of a field sampling program, the most intensive single effort of its kind to date, aimed at the quantification of potentially hazardous pollutants in the waste streams of a representative coal-fired utility boiler. Fuel combustion products that were identified as potentially hazardous air pollutants included 22 trace elements, nitrates, sulfates, polycyclic organic compounds, and polychlorinated biphenyls.

The test facility was a 125-MW boiler at the Tennessee Valley Authority (TVA) Widows Creek steam electric generating station. The boiler, fired with pulverized coal, was equipped with a mechanical fly ash collector. Waste streams sampled included pulverized coal, furnace bottom ash, superheater ash, collection ash and flue gases at the inlet and outlet of the fly ash collection. An integrated sampling train, especially designed and fabricated for this study, was used to collect potentially hazardous particulates and vapors from the boiler flue gases. Collected samples of coal, ash and flue gases were quantitatively analyzed using standard instrumental methods.

Quality assurance checks on the field and laboratory data included complete mass balances on the sampled materials, analyses of duplicate samples, determinations of recoveries from spiked samples, and analyses of certified samples of coal and fly ash from the National Bureau of Standards (NBS).

Significant findings presented in this report include the following:

1. Acceptable mass balance was achieved for about half of the elemental pollutants. The major causes of mass imbalance were: (a) inefficient collection of vaporous metals in the flue gases; and (b) possible analytical errors, particularly in the measurement of trace constituents in coal. With few exceptions, the average mass balance precision was within the expected tolerance (± 25%).

2. Trace metal enrichment was measured: (a) to a moderate degree in cooler ash streams; and (b) to a high degree in the fine particle portion of the fly ash.

Recommendations derived from this study focus on modifications to the methods for collecting and preparing samples. In general, larger and more frequent samples of coal and bulk ash streams are recommended to improve sample representativeness. The need is emphasized for development of methodologies for estimating bulk ash flows, to permit internal checks on the mass balances. Finally, routine chemical analysis of NBS standard coal and fly ash will improve quality assurance of the analytical methods.

SECTION I

CONCLUSIONS AND RECOMMENDATIONS

The conclusions that are derived from this study fall into two subject areas--test methodology and test results. These areas will be discussed separately.

The following study conclusions pertain to the sampling and analysis methods and the operation of the test boiler:

1. The boiler was operating near capacity and otherwise in normal fashion during each of the sampling periods. The excess combustion air averaged about 35% and there was an air infiltration rate of about 25% between the furnace and the stack. The collection efficiency of the mechanical fly ash collector averaged about 45%.

2. Wide variations in physical properties (e.g., color and texture) of grab ash samples, particularly bottom ash and superheater ash, corroborated the large variations in the measured concentrations of trace elements. This suggests potential nonrepresentativeness of composite ash samples consisting of a small number of grab samples.

3. The sampling train designed for collection of potentially hazardous particulates and vapors from the flue gases functioned satisfactorily for most pollutants, but did not efficiently trap vaporous metals (antimony, arsenic, mercury and selenium) because of a loss of oxidizing power of the impinger solution.

4. Analysis of particle size samples for trace metals was limited by the small quantities of particulate collected on the latter impaction stages and on the backup filter.

5. Analysis of duplicate samples indicated good precision in the analytical techniques. However, the average percent recovery of spiked quantities spanned a wider range (80 to 115%). Limited analysis of standard NBS coal and fly ash indicated that determinations of trace metals in ash were more accurate than determinations in coal.

The conclusions which pertain to the calculated results of the Widows Creek sampling study are as follows:

1. With few exceptions, measured mass balance precision was within the expected tolerance of ± 25%. Based on statistical analysis of variance, the major cause of imprecision in mass balance was nonrepresentative sampling; this source of imprecision can be reduced by increasing the sampling frequency and volume sampled.

2. Mass imbalances on the boiler, dust collector and the combination of the two were predominantly negative, indicating that not all of the inlet mass flows could be accounted for in the calculated outlet flows. Inefficient pollutant collection was the major cause of the negative imbalance observed for the vaporous elements (antimony, arsenic, mercury, selenium, and flourine). Mass imbalance was consistently less for the dust collector than for the boiler, reflecting the greater accuracy of pollutant measurement in an ash matrix, and a higher degree of representativeness in the samples collected from the flue gas stream.

3. There was a general tendency for progressive hazardous pollutant enrichment of particulate matter, proceeding from coal through the various ash streams to fly ash at the collector outlet. Exceptions were antimony, barium, beryllium, manganese, tellurium, titanium, and vanadium.

4. Fine particles were found to be enriched with most of the trace metals, with the greatest degree of enrichment occurring for beryllium, cadmium, copper, and zinc. Fine particle enrichment correlated with low removal efficiency by the fly ash collector, as expected.

5. Comparison of flue gas concentrations of trace metals with threshold limit values for industrial exposure indicates that only beryllium is present in sufficient quantity to be of concern as an air pollution health hazard.

As a result of the experience gained in the Widows Creek sampling study, modifications to the methods for collecting and preparing samples are recommended. A modified sampling train designed to efficiently collect inorganic vapors along with particulates and organic vapors is recommended for the collection of potentially hazardous pollutants from the boiler flue gases. An alternate sampling train developed by TRW is currently being used by KVB Engineering to sample hazardous emissions from industrial boilers. Neither of these trains has been adequately field tested at this time.

Because of the large short-term variations in the trace constituent composition of coal and bulk ash streams, both sample size and frequency should be increased to reduce the variance of mass balance. The frequency of sampling corresponding to a desired tolerance may be determined by reworking the statistical model presented. Sample size must more closely conform with the specifications of Method D2234 of the American Society for Testing and Materials. In addition, methods should be developed for directly estimating the flows of bulk ash streams.

In the Widows Creek study, it was assumed that soot buildup on the boiler tubes had the same composition as superheater hopper ash, and that soot plus superheater ash amounted to 20% of the input coal ash. More data are needed to determine the rate of soot buildup and samples should be obtained, if possible, for chemical analysis.

A smaller digestion bomb should be used for treatment of samples from the Brink impactor. MRI has designed a bomb with a 5-ml volume, one-tenth of the volume used in the Widows Creek study. This device will facilitate treatment of small samples and transfer of the 1-ml sample for analysis by atomic absorption spectrophotometry.

Finally, it is recommended that NBS coal and fly ash standards be analyzed routinely along with field samples collected in future studies, to improve quality assurance of the analytical methods.

SECTION II

INTRODUCTION

BACKGROUND

Recent studies of the hazardous air pollutant problem* have indicated that fossil fuel combustion in utility boilers is a major contributing source.[1-5] This conclusion has been based primarily upon the knowledge that coal and oil contain a variety of potentially hazardous trace metals which may be discharged into the atmosphere in the combustion waste gas stream. In addition, the incomplete combustion of organic fuel is a source of polynuclear compounds which are known carcinogens.[6] These conclusion have been reinforced by limited measurements of hazardous constituents in power plant emissions, primarily in fly ash.

The environmental impact of hazardous pollutants generated by fossil fuel combustion in utility boilers is potentially much greater than the relative mass emissions would suggest, because some pollutants may be emitted in the form of vapors or fine particulates which penetrate the customary particulate pollutant control devices as well as the conventional source sampling instruments. The emissions of hazardous pollutants as fine particulates (and vapors) intensify the potential adverse health effects for two reasons: (a) pollutants in this form penetrate the natural filters of the respiratory tract, and reach the air spaces of the lung; and (b) fine particle emissions, largely formed by condensation of volatile materials, are enriched in toxic elements in comparison to the average composition of the earth's crust (a measure of the acceptable metabolic tolerance level in humans).

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* Section 112 of the Clean Air Act defines hazardous pollutants as those which may cause or contribute to an increase in mortality or an increase in serious irreversible or incapacitating reversible illness.

PROGRAM OBJECTIVE

EPA's Control Systems Laboratory has the responsibility to develop technology to control hazardous emissions from utility boilers. Necessarily, the control program must be based on field measurements which adequately characterize and quantify the potentially hazardous vapors and particulates in utility boiler waste gases. In the absence of definitive data of this type, two primary objectives were set for this investigative program:

1. The development of a comprehensive plan for measuring potentially hazardous constituents in representative utility boiler exhaust streams.

2. The field implementation of the test plan at a full-scale utility boiler of representative design and operation.

The original intent of this program was to draw upon previously documented studies in the formulation of the plan for field sampling of utility boilers and for chemical analysis of collected samples. However, in the early stages of the program, the recognition of the inadequacies of currently available information (relative to the scope of the required testing effort) necessitated a shift in emphasis from method application to method development.

Consequently, a major objective of the initial (field) effort to implement the test plan was the investigation of the reliability and accuracy of the sampling and analysis methods. TVA's Widows Creek coal-fired steam-electric power plant was selected for the test program.

RELATED STUDIES*

Little pertinent data are available from previous or current multielement studies of trace materials in boiler waste gases. Until about 1970, particulate pollutant sampling and analysis methods were not sufficiently refined to permit the accurate determination of trace constituents in fly ash. Furthermore, techniques for sampling volatile trace materials in the vapor or fine aerosol state are just now being developed.

---

* This literature review was conducted in mid-1974; other pertinent field studies have been initiated more recently.

One current program of interest is Oak Ridge National Laboratory's investigation of the disposition of trace elements from coal combustion at the TVA Thomas A. Allen Steam Plant in Memphis, Tennessee.[3,7] The test boiler, which drives a 290 MW generating unit, is cyclone-fed with crushed coal. (Unfortunately, this firing method represents only 9% of the total generating capacity of coal-fired utility boilers.) Mass balance data and the collection efficiency of a new electrostatic precipitator have been determined for 34 elements including many trace constituents. Samples of particulates collected with a cascade impactor are being analyzed to determine trace element concentration as a function of particle size.

In another study, by the University of Colorado, data have been collected on the distribution of 16 particulate trace elements in the waste streams of a 180 MW generating unit fired with pulverized coal, at the Valmont Power Plant near Boulder, Colorado.[8] Particulate emissions from the test boiler were controlled with a mechanical collector followed by an electrostatic precipitator in parallel with a wet scrubber. However, no data on particle size or particulate collection efficiency were reported.

In other related work, the Edison Electric Institute is sponsoring a study at the Battelle Memorial Institute to obtain a mass balance for 14 critical elements around an experimental boiler facility fired with either pulverized coal or residual oil. Battelle has also conducted a recent project for EPA to determine the effect of alternative sampling techniques on the amount and composition of particulates measured in the effluent gases of oil- and coal-fired combustion sources.[9] In conjunction with this latter work, approximate trace element analysis was performed on fly ash samples collected at the inlet and outlet of an ESP which controlled emissions from a pulverized coal-fired boiler at the Edgewater Power Plant in Loraine, Ohio.

Finally, the EPA has maintained interest in the fate of trace elements in relation to various SO_2 removal demonstration projects. For example, as subcontractor to the MITRE Corporation on the Cat-Ox demonstration program, MRI collected coal ash samples and measured the concentrations of some 28 elements in the waste streams of a pulverized coal-fired boiler with a mechanical collector.[10] The test boiler drove a 100 MW generator at Illinois Power Company's Wood River, Illinois, plant.

The remainder of this report is organized as follows:

Section	Subject
III	Potentially Hazardous Pollutants Generated by Utility Boilers
IV	Typical Boiler Characteristics and Flue Gas Environment
V	The Test Plan for Field Sampling and Chemical Analysis of Hazardous Emissions from Representative Utility Boilers
VI	The Widows Creek Test Boiler and Associated Sampling Program
VII	Analytical Results from the Widows Creek Program
VIII	Test Results Calculated from Laboratory and Field Data

SECTION III

HAZARDOUS POLLUTANTS FROM FOSSIL FUEL COMBUSTION

The first major task in this program was to develop a list of potentially hazardous pollutants originating from fossil fuel combustion in utility boilers. To accomplish this, several lists of hazardous pollutants from MRI's literature files were combined to form a master list, which in turn was checked against information on the trace elements in coal and fuel oil consumed by power plants.

HAZARDOUS CONSTITUENTS IN UTILITY BOILER FUEL

As the first step in the determination of representative concentrations of trace elements in utility boiler fuels, the origin of coal[11] and residual fuel oil[12] consumed by utility boilers was determined. It was found that: (a) nearly all of the coal consumed by power plants comes from two coal mining regions of the country: the Appalachian (56%) and Interior Eastern (34%) regions (Table 1) (the percentage of coal consumption originating from the western region increased from 5.0% in 1970 to 6.7% in 1972[12a]); and (b) most of the domestic crude oil originates from three states--Texas, Louisiana, and California (Table 2) (of the total amount of crude oil processed in the United States, approximately 85% is produced domestically with the balance being imported[13]).

Next, the most reliable information available on the potentially hazardous elements in coal and oil[13] was analyzed to determine representative concentrations in the fuel from each producing region. Figure 1 gives the extremes in average concentration of trace elements for over 90% of the beds within each coal producing region. It is important to note that for most trace elements, the variations of concentration within a coal bed are frequently greater than the differences between the averages for different beds.[13] The information on the origin of residual fuel oil and the hazardous constituents in oil was much less complete than the information on coal; however, the data for residual fuel oil are less critical because oil accounts for only 20% of the Btu output from utility boilers.[14]

Table 1. ORIGIN OF COAL CONSUMED BY ELECTRIC UTILITIES IN 1970 11/

Origin of Coal		Consumption a/ (thousand short tons)	
District	Region	Electric Utilities	Total
1 - Pennsylvania, Maryland, West Virginia	A	31,089	46,647
2 - Pennsylvania	A	8,804	39,581
3 and 6 - West Virginia	A	36,809	50,053
4 - Ohio	A	41,893	55,699
7 - Virginia, West Virginia	A	1,192	37,128
8 - Kentucky (east), Tennessee (east), Virginia, West Virginia	A	62,009	161,022
9 - Kentucky (west)	IE	47,844	53,360
10 - Illinois	IE	50,745	67,660
11 - Indiana	IE	15,956	22,641
12 - Iowa	IW	812	882
13 - Alabama, Tennessee (west)	A	11,296	20,511
14 - Arkansas	IW	--	1,000
15 - Kansas, Missouri, Oklahoma	IW	6,981	7,625
16 - Colorado	SW	522	593
17 - Colorado, New Mexico	SW	2,357	6,602
18 - New Mexico, Arizona	SW	6,525	6,498
19 - Wyoming	W	6,405	7,215
20 - Utah	SW	1,005	4,586
21 - North Dakota, South Dakota	N	4,870	5,916
22 - Montana	N		
23 - Washington, Alaska	N + Alaska	2,237	2,773
Total		339,351	597,992

---

a/ Total Electric Utility Consumption by Coal Source Region, in thousand short tons.

Appalachian (A)	193,092
Interior - Eastern (IE)	114,545
Interior - Western (IW)	7,793
Western (W)	16,814
Southwestern (SW)	(10,409)
Northern (N)	7,107
Total	339,351

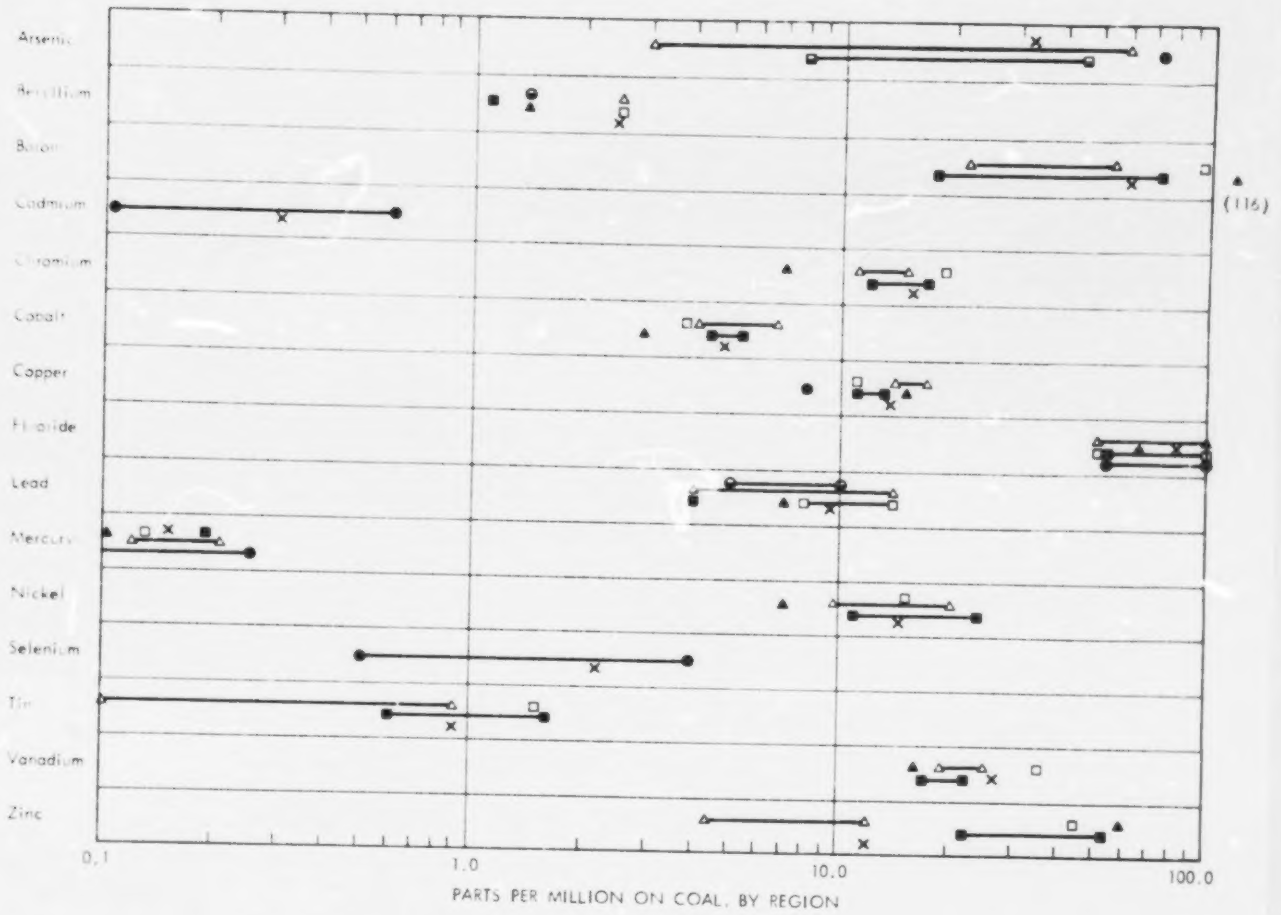
Table 2. TRACE ELEMENTS IN U.S. CRUDE OIL (Parts Per Million)[13]

Element	Origin of Crude California	Louisiana	Texas	Weighted Average[a]
Antimony	< 0.007	0.05	< 0.01	< 0.024
Arsenic	< 0.007	0.05	< 0.12	< 0.08
Barium	< 0.06	0.09	< 0.14	< 0.11
Manganese	0.018	0.027	< 0.05	< 0.04
Nickel	77	4.4	3.3	16
Tin	< 0.6	0.5	< 1.0	< 0.8
Vanadium	48	1	1.9	9.0

---

[a] From Petroleum Facts and Figures 1971[12]

State	1968 Production (1,000 barrels)	% of U.S. Production
California	375,496	11.28
Louisiana	817,426	24.55
Texas	1,133,380	34.05
		69.88



LEGEND

Symbol	Region	States Included
△	Appalachian (A)	Pennsylvania, Ohio, West Virginia, Maryland, Virginia, Eastern Kentucky, Tennessee, Alabama (and Georgia)
□	Interior-Eastern (IE)	Illinois, Indiana, Western Kentucky, Michigan
■	Interior-Western (IW)	Iowa, Missouri, Nebraska, Kansas, Oklahoma, Arkansas, Texas
○	Western (W)	Wyoming, Idaho, Utah, Colorado, New Mexico, Arizona, Washington
●	Southwestern (SW)	Utah, Colorado, Arizona, New Mexico
▲	Northern Great Plains (N)	Montana, North Dakota, South Dakota
×	Region Average	(weighted by amount of coal from each region consumed by utility boilers)

Figure 1. Trace element concentrations in coal.13/

Finally, representative concentrations of trace elements in utility boiler fuel (Table 3) were derived by weighting the average concentrations for each coal or oil producing region by the amount of fuel from that region which is consumed by utility boilers. Also shown in Table 3 are emission factors based on average heating values.

Although little information is available on hazardous organic constituents in utility boiler emissions, there is strong reason to suspect that polycyclic organic material (POM) and possibly polychlorinated biphenyls (PCB) are formed during combustion of fossil fuels and escape to the atmosphere prior to complete oxidation. Benzo[a]pyrene, one of the key carcinogens present in the atmosphere, has been specifically measured in power plant waste gases.10,15,16/ Other POM with high carcinogenicity ratings are indicated in Table 4.

HAZARDOUS POLLUTANT IMPACT RATING

The relative potential environmental impact of hazardous pollutants generated by utility boilers depends on three factors:

1. The amount of pollutant potentially liberated to the flue gas stream per unit of heat input.

2. The volatility of the pollutant or its tendency to exist in flue gases as a vapor or fine particulate.

3. The inherent toxicity of the pollutant.

Data on the volatility of trace constituents were obtained from a recent study of the retention of elements during the oxidation of coal at various temperatures.18/ The boiling point of the pure elements was also taken as a measure of its volatility.7/ Finally, for the elements treated in the experimental studies cited above,3,7,8/ further indicators of high volatility were taken to be: (a) high negative mass imbalance; (b) fine particle enrichment; or (c) high relative mobilization to flue gases (Table 5).

Scientific judgment was used in developing the volatility classification from all of the applicable evidence; the results are shown in Table 6. The temperature range of interest for the identification and control of hazardous pollutants is 200 to 800°F.

Table 3. TRACE ELEMENTS IN FOSSIL FUELS CONSUMED BY ELECTRIC UTILITIES

Element	Coal			Oil	
	Concentration[a] (ppm)	Variance[b]	Emission Factor $(g/10^6$ Btu$)$[c]	Concentration[a] (ppm)	Emission Factor $(g/10^6$ Btu$)$[d]
Antimony	5[e]		0.20	< 0.024	0.0059
Arsenic	32		1.3	< 0.08	0.002
Barium	500[e]		20.2	< 0.11	0.003
Beryllium	2.44	5	0.099		
Boron	61	6	2.47		
Cadmium	0.03		0.001		
Chlorine	160		6.48		
Chromium	15.4	2	0.624		
Cobalt	4.8	2	0.194		
Copper	13.5	1.5	0.547		
Fluorine	82	3	3.32		
Lead	9.5	3	0.38		
Manganese	50[e]		2.02	< 0.04	0.001
Mercury	0.15	3	0.0061		
Nickel	14.8	3	0.599	16	0.39
Selenium	2.2		0.089		
Tellurium	1[e]		0.04		
Thallium	0.3[e]		0.01		
Tin	0.9	>3	0.036	< 0.8	0.02
Titanium	385		15.6		
Vanadium	26.4	2	1.07	9	0.22
Zinc	12	>5	0.49		

---

a/ Source: Potential Pollutants in Fossil Fuels.[13]

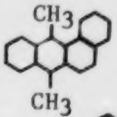
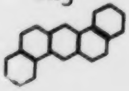
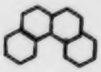
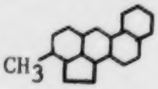
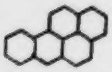
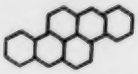
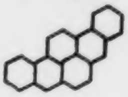
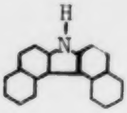
b/ Ratio of highest to lowest averages, for coal regions or areas.

c/ Based on heating value of 11,200 Btu/lb for coal as burned.[14]

d/ Based on heating value of 18,400 Btu/lb for residual oil as burned.[14]

e/ Estimated values based on data from various sources.[3,15,17]

Table 4. CARCINOGENIC POLYCYCLIC ORGANIC MATERIALS

Compound	Structure	Carcinogenicity[a/]
1. 7,12 Dimethylbenz[a]-anthracene		+ 4
2. Dibenz[a,h]anthracene		+ 3
3. Benzo[c]phenanthrene		+ 3
4. 3 Methylcholanthrene		+ 4
5. Benzo[a]pyrene		+ 3
6. Dibenzo[a,h]pyrene		+ 3
7. Dibenzo[a,i]pyrene		+ 3
8. Dibenzo[c,g]carbazole		+ 3

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a/ Taken from Ref. 6; compounds of highest carcinogenicity, (4 > 3 > 2...) from a list of over 50 compounds rated from (-) to (+ 4).

Table 5. MASS BALANCE RESULTS--CYCLONE-FED BOILER[3]

Element	Analysis Method[a]	Mass Flow (gm/min)		% Mobilized to Flue Gases
		Coal	Slag Tank	
Arsenic	NAA	4.7	0.05	99
	SSMS	6.2	0.22	96
Barium	NAA	99	66	33
	SSMS	130	33	75
Beryllium	SSMS	< 6.3	< 1.1	~83
Boron	SSMS	250	33	87
Cadmium	SSMS	0.63	0.22	65
Chromium	NAA	26	20	23
	SSMS	37	< 22	> 40
Cobalt	NAA	4.1	2.1	49
	SSMS	9	4.4	51
Copper	SSMS	63	22	65
Lead	SSMS	< 25	0.33	< 99
Manganese	NAA	67	46	31
	SSMS	130	110	15
Mercury	AAS	0.079	0.0099	87
Nickel	SSMS	≤ 130	55	≤ 58
Selenium	NAA	4.0	1.5	62
Titanium	NAA	890	330	63
	SSMS	880	220	75
Vanadium	NAA	26	14	46
	SSMS	37	11	70
Zinc	SSMS	110	11	90

---

[a] NAA = Neutron Activation Analysis (±10%)
SSMS = Spark Source Mass Spectroscopy (±50%)
AAS = Atomic Absorption Spectroscopy (±5%)

Table 6. VOLATILITY OF TRACE ELEMENTS IN COAL

Volatility Index and Temperature[a,b]

1	2	3	4	5
< 300°F	300-850°F	850-1300°F		> 1300°F
mercury	selenium	zinc[c]	copper	beryllium
fluorine	arsenic	- - - - -	cobalt	boron
thallium	- - - - - -	barium[c]	lead	titanium
antimony	chlorine		manganese	
	tellurium		nickel[d]	
			chromium[d]	
			cadmium[e]	
			vanadium	
			- - - - - -	
			tin	

---

a/ Entries above dashed lines are from Occurrence and Distribution of Potentially Volatile Trace Elements in Coal.[18]

b/ Temperature ranges within which volatilization of an element occurs.

c/ Preferentially concentrated in fine particles of fly ash (pulverized firing).[7]

d/ Concentrated in crust of moderate-sized particles of fly ash (pulverized firing).[7]

e/ Large percentage to bottom ash (pulverized firing).[7]

The relative toxicity index of each constituent was based on the threshold limit values determined by the American Conference of Governmental Industrial Hygienists[19] and on the review article by Dr. H. A. Schroeder.[17]

Table 7 presents the impact ranking based on concentration, volatility, and toxicity of each potentially hazardous element. In the composite ranking, toxicity has been given more weight than the other two factors. Note that boron was eliminated from further consideration because of its low impact ranking coupled with inherent difficulties in chemical analysis procedures. It was judged that the added costs of boron analysis were not justified by the relative significance information to be gained.

The remainder of this document focuses on coal-fired boilers which account for 80% of the Btu output of utility boilers.[14]

Table 7. HAZARDOUS POLLUTANT IMPACT RANKING

Element	Concentration in Fuel		Volatility Index[c]	Toxicity Index[d]	Composite Index[e]	Impact Ranking
	$g/10^6$ Btu[a]	Index[b]				
Antimony	0.16	3	1-2	3	40	7
Arsenic	1.04	2	2	3	36	6
Barium	16.2	1	3	4[f]	48	9
Beryllium	0.079	4	5	1	20	1
Boron	1.98	2	5	5	250	21
Cadmium	0.0008	5	4	2	80	12
Chlorine	5.2	2	2	4	64	11
Chromium	0.50	3	4	3	108	14
Cobalt	0.15	3	4-5	2-3[f]	84	13
Copper	0.44	3	4	3	108	14
Fluorine	2.66	2	1	3-4	24	4
Lead	0.30	3	4	2	48	9
Manganese	1.62	2	4	4	128	20
Mercury	0.005	5	1	2[f]	20	1
Nickel	0.56	3	4	3	108	14
Selenium	0.071	4	2	2	32	5
Tellurium	0.032	4	2-3	2	40	7
Thallium	0.0096	5	1	2	20	1
Tin	0.033	4	4	4	256	22
Titanium	12.5	1	4-5	5	112	19
Vanadium	0.90	3	4	3[f]	108	14
Zinc	0.39	3	3	3-4	110	18

---

a/ Concentration factors for coal and oil (Table 3) weighted 4 to 1, respectively.

b/ $1 = > 10$ $g/10^6$ Btu, 2 = 1-10, 3 = 0.1-1, 4 = 0.01-0.1, $5 = < 0.01$.

c/ See Table 6 for index categories.

d/ 1 = Extremely toxic, threshold limit value (TLV) < 0.1 mg/m^3; 2 = Highly toxic, $0.1 \leq TLV < 0.5$; 3 = Very toxic, $0.5 \leq TLV < 2$; 4 = Toxic, $2 \leq TLV < 15$; 5 = Mildly toxic, $TLV \geq 15$.

e/ Composite = $(Toxicity)^2$ x Volatility x Concentration.

f/ Value adjusted from information in Reference 17.

SECTION IV

CHARACTERISTICS OF UTILITY BOILERS AND FLUE GAS ENVIRONMENT

The typical coal-fired steam-electric plant is comprised of a boiler, generator, condenser, fuel handling equipment, dust collection and disposal equipment, water handling and treatment facilities, and heat recovery systems such as economizers and air heaters. A simplified process schematic is given in Figure 2.

BOILER CHARACTERISTICS

The major design characteristics which differentiate utility boilers are: (a) fossil fuel type; (b) method of firing; (c) furnace temperature; (d) gross generating capacity; and (e) air pollution control equipment. Each of these factors will be discussed below.

Method of Firing

The mechanical firing methods for coal-fired boilers in present day usage include pulverized, cyclone (utilizing a coarser mix of pulverized coal), and stoker types, with pulverized firing comprising nearly 90% of the total. Figure 3 shows the relative prevalence of firing methods, as derived from a recent (9 January 1974) National Emissions Data System (NEDS) listing.[20/] Boilers fired with pulverized coal are classified with respect to the firing position of the burners as shown in Figure 4.[21/] Figure 5 shows the prevalence of pulverized-coal firing method as a function of boiler size, based on recent data provided by the Edison Electric Institute (EEI).[22/]

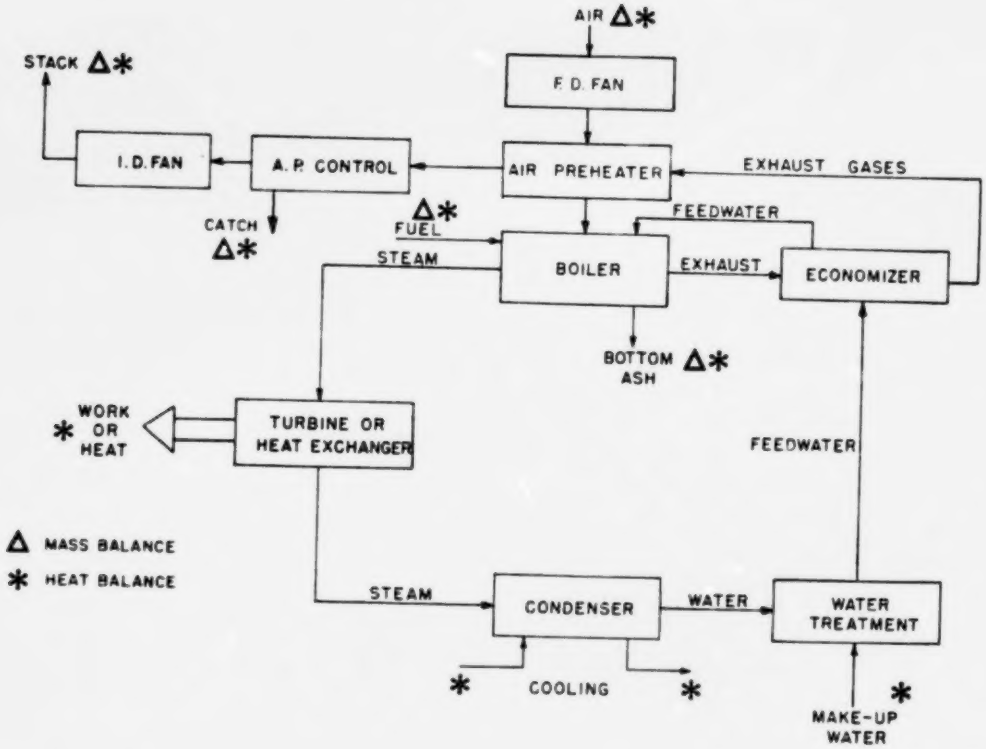
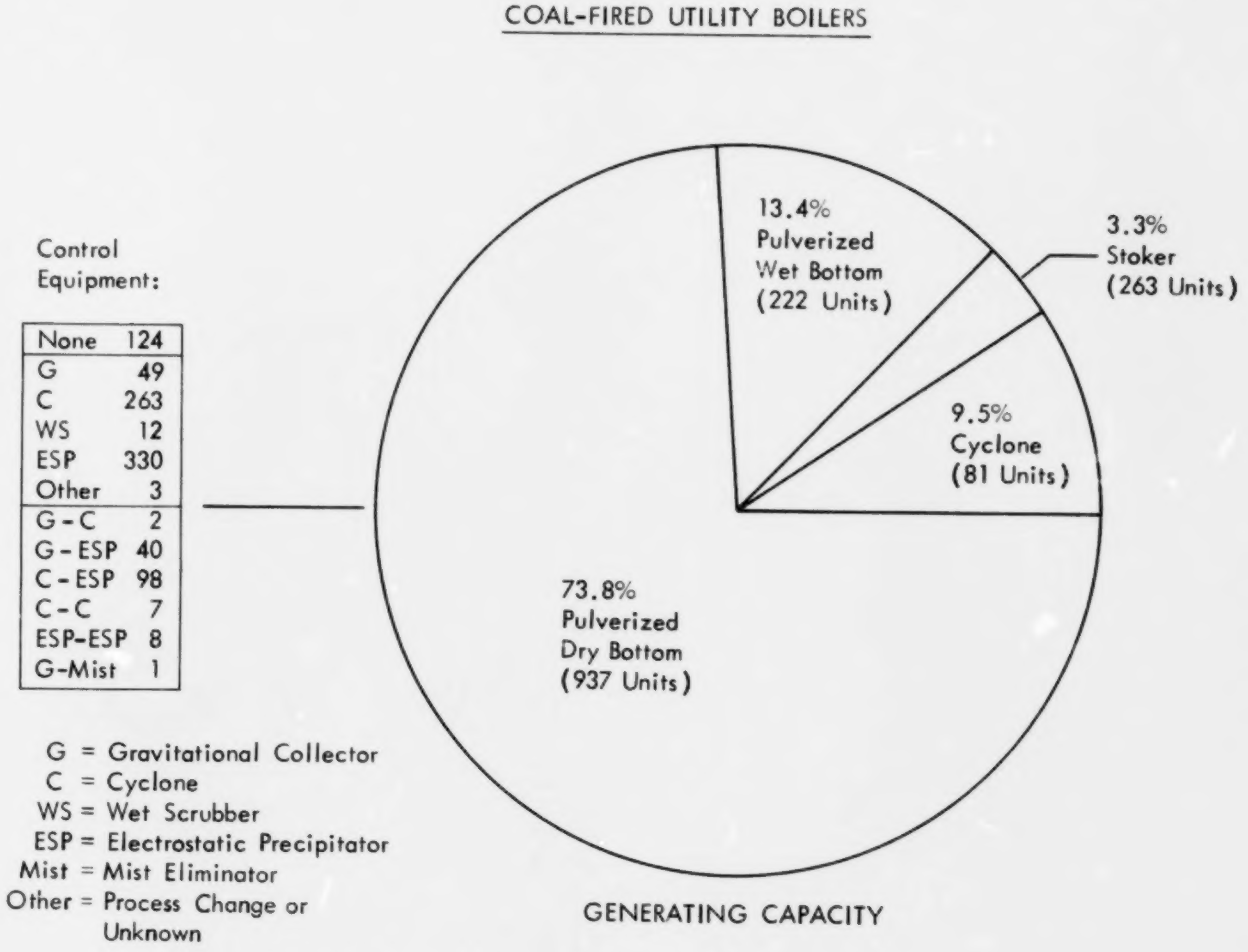

AIR Δ*
STACK Δ*
F.D. FAN
I.D. FAN
A.P. CONTROL
AIR PREHEATER
EXHAUST GASES
CATCH Δ*
FEEDWATER
Δ*
FUEL
STEAM
BOILER
EXHAUST
ECONOMIZER
BOTTOM ASH Δ*
* WORK OR HEAT
TURBINE OR HEAT EXCHANGER
FEEDWATER
Δ MASS BALANCE
* HEAT BALANCE
STEAM
CONDENSER
WATER
WATER TREATMENT
* COOLING *
*
MAKE-UP WATER

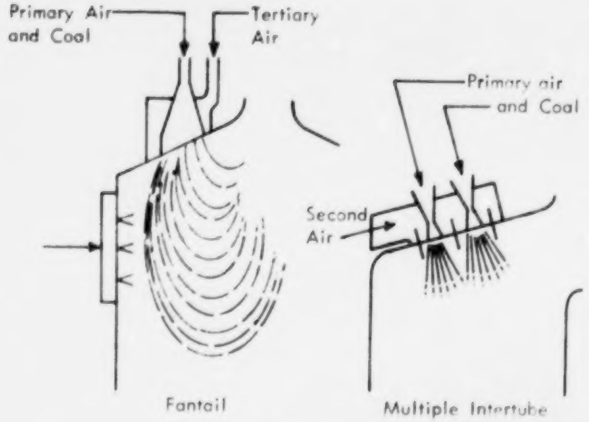
Figure 2. Simplified process diagram for steam-electric generator.



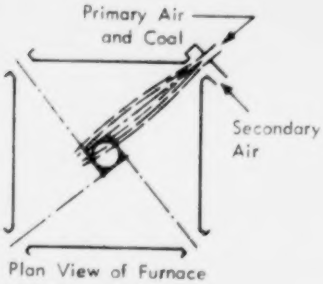
None	124
G	49
C	263
WS	12
ESP	330
Other	3
G - C	2
G - ESP	40
C - ESP	98
C - C	7
ESP-ESP	8
G-Mist	1

G = Gravitational Collector
C = Cyclone
WS = Wet Scrubber
ESP = Electrostatic Precipitator
Mist = Mist Eliminator
Other = Process Change or Unknown

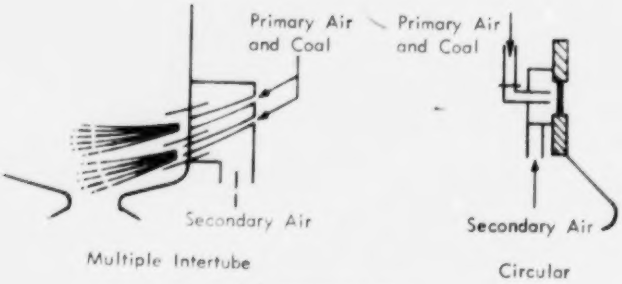
Figure 3. Prevalence of coal-firing methods.20/


Primary Air and Coal
Tertiary Air
Primary air and Coal
Second Air
Fantail
Multiple Intertube

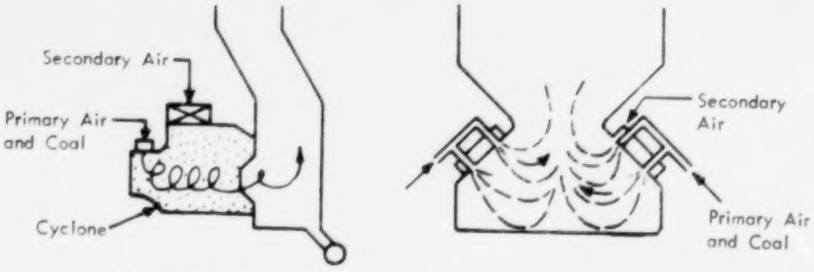
(a) Vertical Firing


Primary Air and Coal
Secondary Air
Plan View of Furnace

(b) Tangential Firing


Primary Air and Coal
Primary Air and Coal
Secondary Air
Secondary Air
Multiple Intertube
Circular

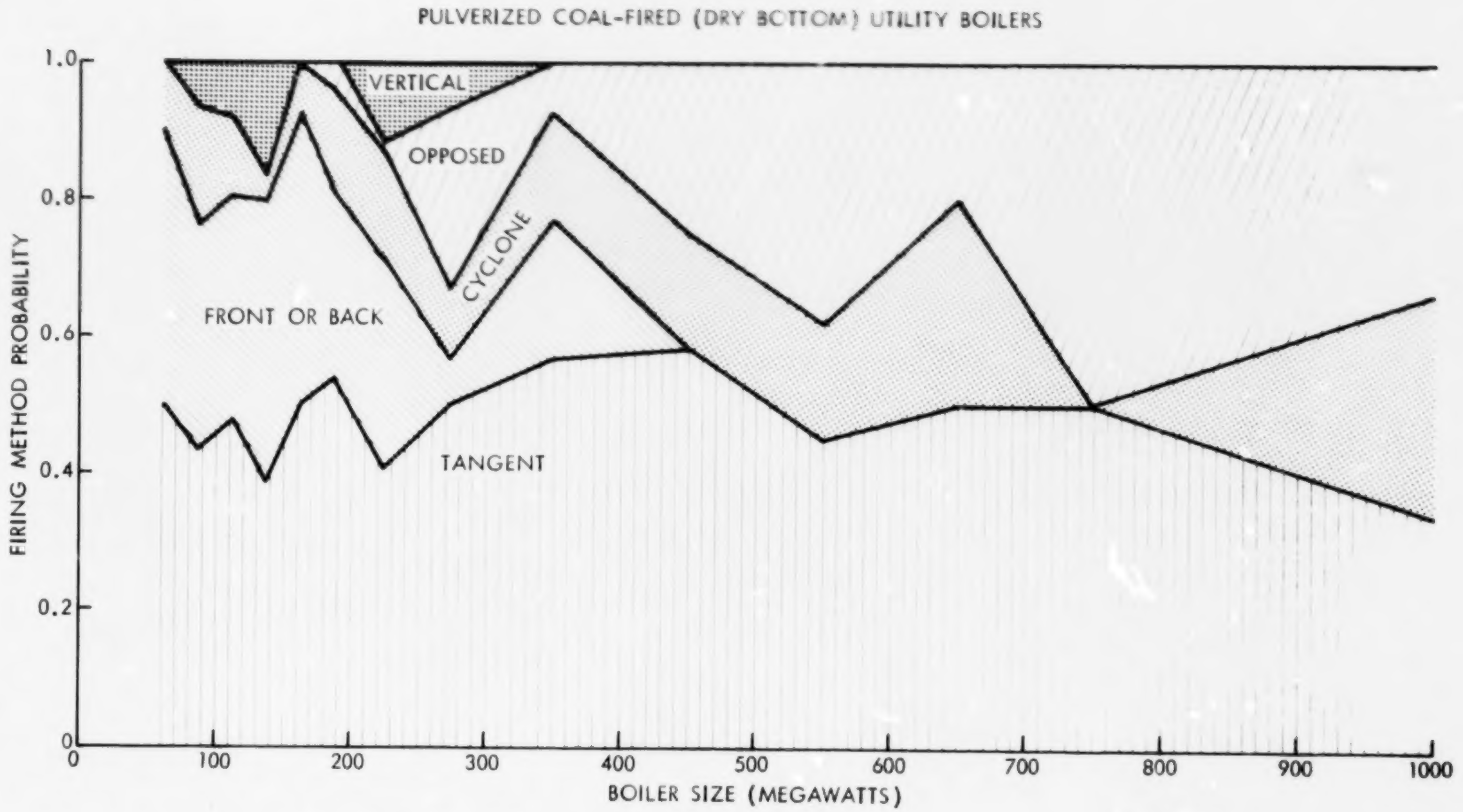
(c) Horizontal Firing


Secondary Air
Primary Air and Coal
Cyclone
Secondary Air
Primary Air and Coal

(d) Cyclone Firing

(e) Opposed-Inclined Firing

Figure 4. Pulverized coal-firing methods.21/



Vertical and Front or Back not in larger boilers
Opposed not in smaller boilers

Figure 5. Firing method vs boiler size.[22]

For the most part, the burner configuration in units fired with pulverzied coal does not in itself have a major effect on emission characteristics.[23] However, based on limited data which show that the amount of unburned combustibles in the coal ash is affected by method of firing,[15,16,23] it is likely that the firing method may have a substantial effect on the generation of POM's. The controlling factors appear to be furnace temperature distribution and residence time.

Furnace Temperature

Pulverized coal-fired boilers are also classified as either wet-bottom (slag-tap) or dry-bottom, depending on the furnace temperature relative to the ash fusion temperature. All cyclone-type furnaces are wet-bottom.

Gross Generating Capacity

Utility boilers may be categorized by size as shown in Table 8. The trends in the average size of fossil-fueled steam-electric generators in this country are depicted in Figure 6.[24] In 1968, the average size steam-electric unit was 66 MW, but the average size of utility boilers under construction in 1970 was 460 MW. (Since 1950 it has been common practice to have one boiler per turbine generator.[24])

From recent inventories of utility boilers, the size distribution of the "current" population of pulverized coal-fired (dry-bottom) utility boilers has been derived. Figure 7 shows the distribution for boilers larger than 50 MW and Figure 8 for all utility boilers, based on a recent (9 January 1974) NEDS inventory.[20] From these figures it is evident that the boiler population closely follows a log-normal size distribution. Also shown in Figure 7 is a size distribution for pulverized coal-fired utility boilers derived from the EEI inventory.[22]

Air Pollution Control Equipment

The most common types of particulate emission control equipment for coal-fired utility boilers are centrifugal collectors and electrostatic precipitators. Table 9 gives the distribution of control equipment currently in use on coal-fired utility boilers, based on a recent listing from the National Emissions Data System.[25]

Table 8. SIZE CATEGORIES FOR STEAM-ELECTRIC POWER PLANTS

	Large	Intermediate	Small
Btu per hour	$\geq 5 \times 10^8$	$3 \times 10^5 - 5 \times 10^8$	$< 3 \times 10^5$
Boiler horsepower	≥ 15,000	10-15,000	< 10
Pounds of steam per hour	≥ 500,000	350-500,000	< 330
Megawatts	≥ 50	< 50 MW	Not applicable

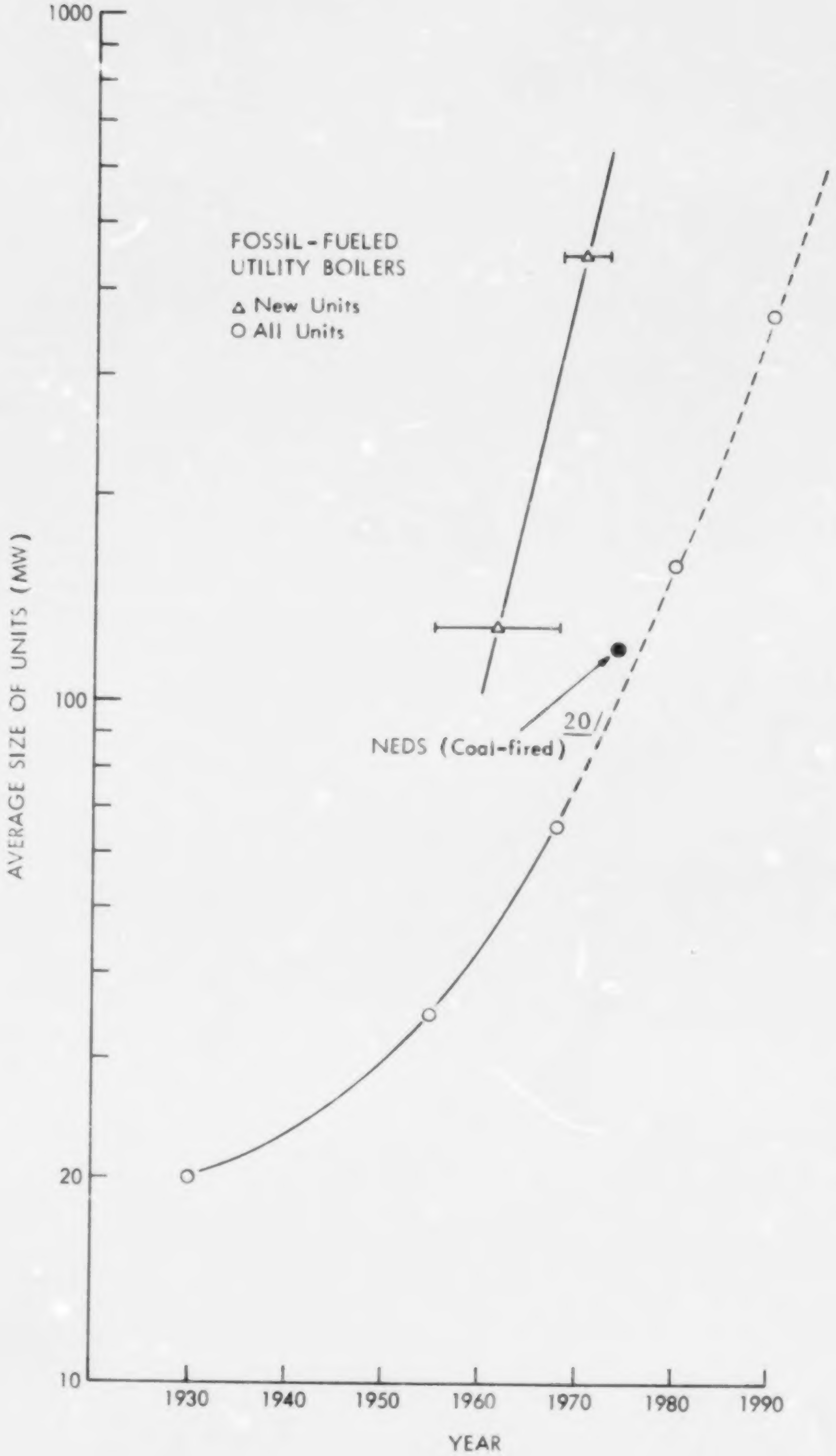


Figure 6. Trends in utility boiler size.[24/]

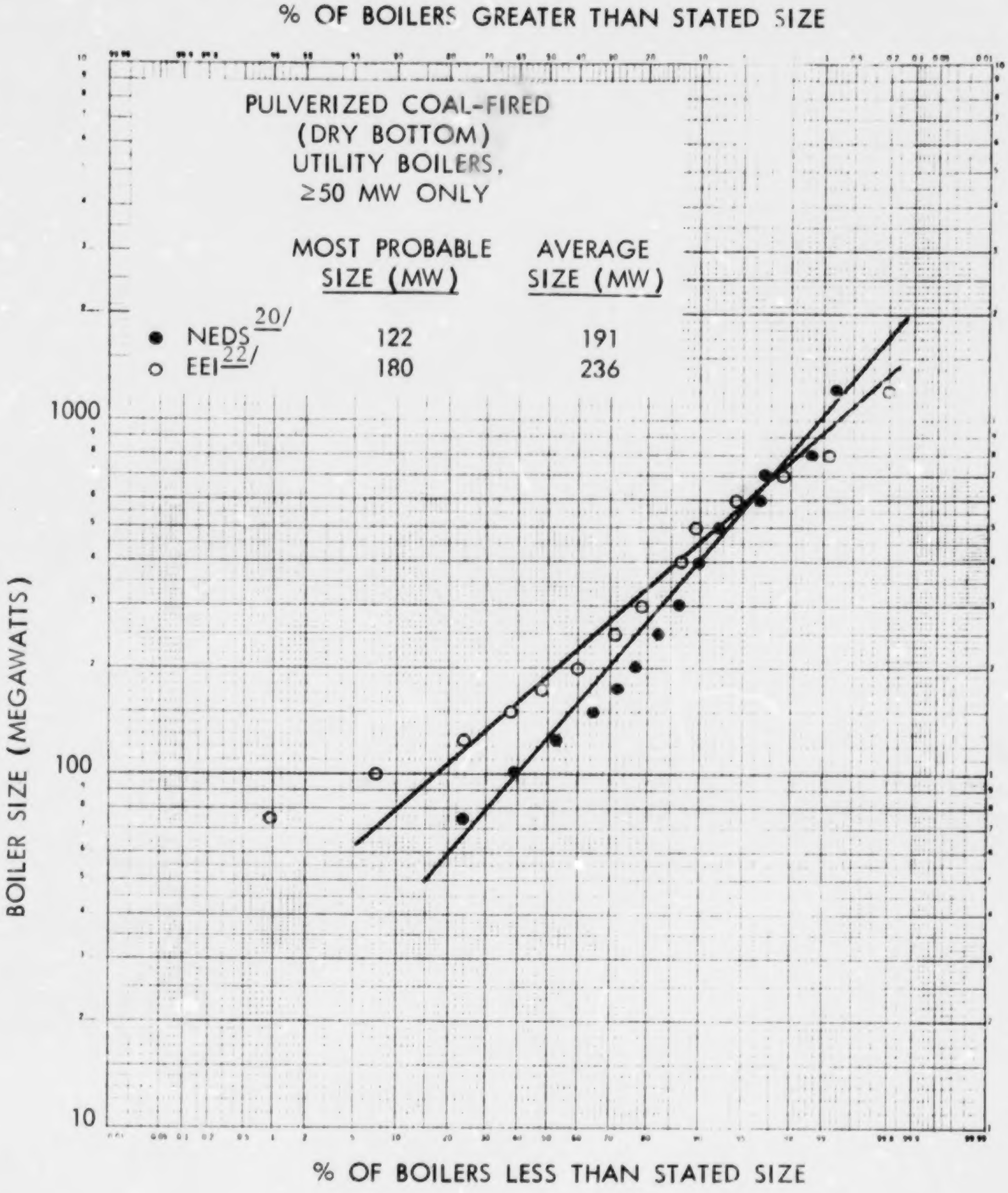


Figure 7. Utility boiler size distribution (≥ 50 MW).

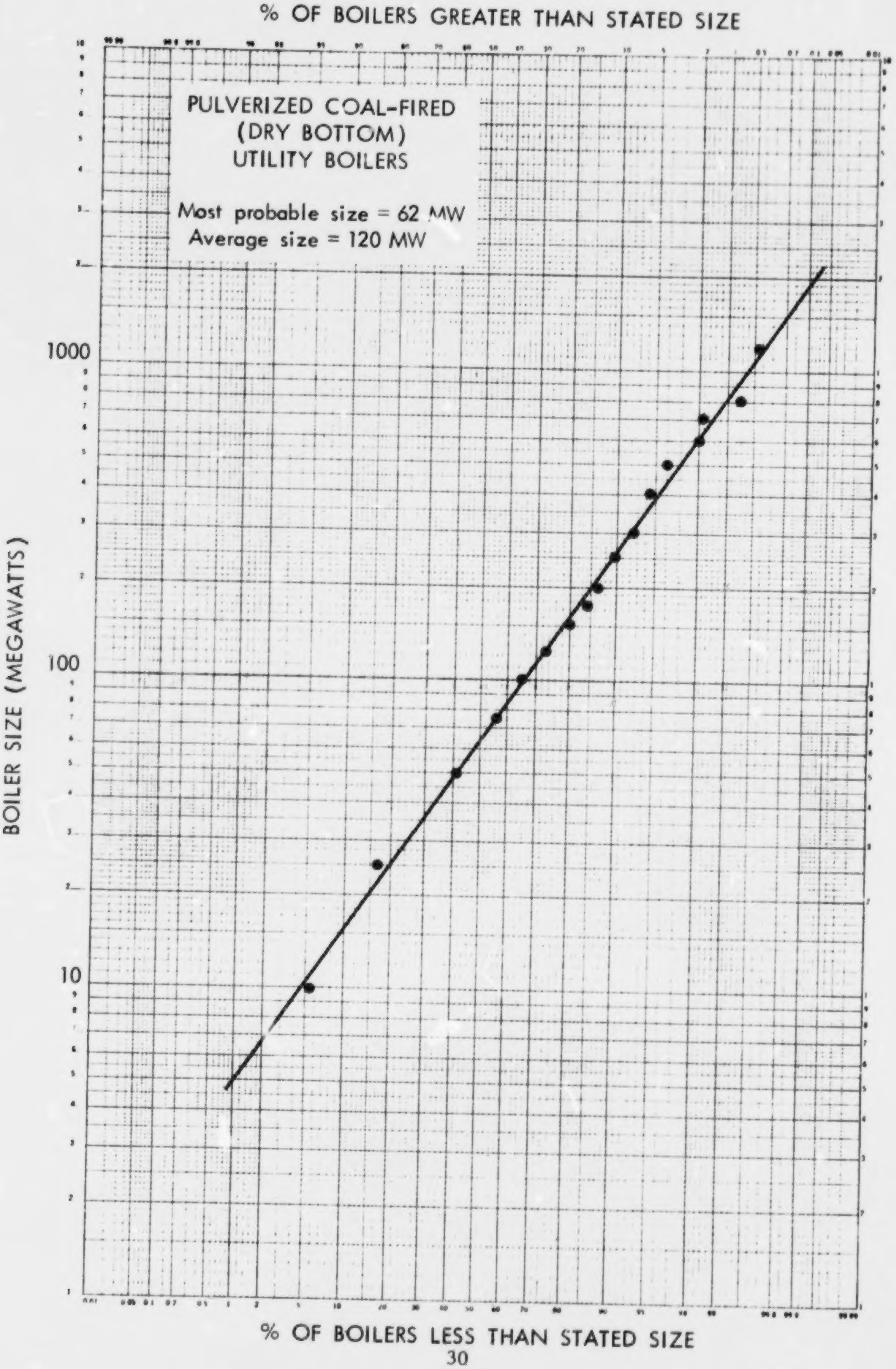


Figure 8. Utility boiler size distribution.[20]

Table 9. PARTICULATE EMISSION CONTROL EQUIPMENT
(Coal-Fired Utility Boilers[a])

Boiler Type (Firing)	Number of Emission Sources, by Control Type					
	No Control	Gravitational Collector	Centrifugal Collector	Electrostatic Precipitator	Wet Scrubber	Total
Pulverized - Dry Bottom	108	83	355	330	10	886
Pulverized - Wet Bottom	40	3	76	87	4	210
Cyclone	15	1	15	48	3	82
Stoker	28	15	77	1	0	121
TOTAL	191	102	523	466	17	1,299

---

[a] Boiler size > 100 million Btu/hr (10 MW).
Source: NEDS listing, dated 8/23/73.[25]

Figure 9 is a boiler characteristics "tree" which was developed from a NEDS utility boiler inventory (9 January 1974).[20/] It divides the current coal-fired boiler population into firing types and gives detailed information on the pulverized dry-bottom segment of the population. For each specified size range of pulverized dry-bottom boilers, the figure specifies:

1. The percentage of the total generating capacity of coal-fired utility boilers.

2. The number of boilers (indicated on the outer branches).

3. The distribution of particulate emission control devices.

Figure 10 presents the distribution of control devices as a function of boiler size.

The emerging technologies for the control of gaseous emissions from utility boilers should also be considered as potential sources of hazardous emissions. Flue gas desulfurization systems are increasing in number throughout the electric utility industry and will soon have a substantial effect on utility boiler emissions.

In addition to fuel characteristics, the most important process parameters in utility boiler operation are: (a) load facfactors (percentage of rated boiler capacity at any point in time); (b) excess air; and (c) soot blowing cycle. For a given boiler, the furnace temperature is determined by the first two of these parameters.

FLUE GAS ENVIRONMENT

As flue gases travel from the point of generation to the point of atmospheric discharge, two important changes take place: (a) the temperature drops from near 3000°F to about 300°F and (b) most of the large particles of fly ash are removed by a particulate collection device.

The temperature history of the flue gases (Figure 11) has a major effect on the physical and chemical form of potentially hazardous flue gas constituents.

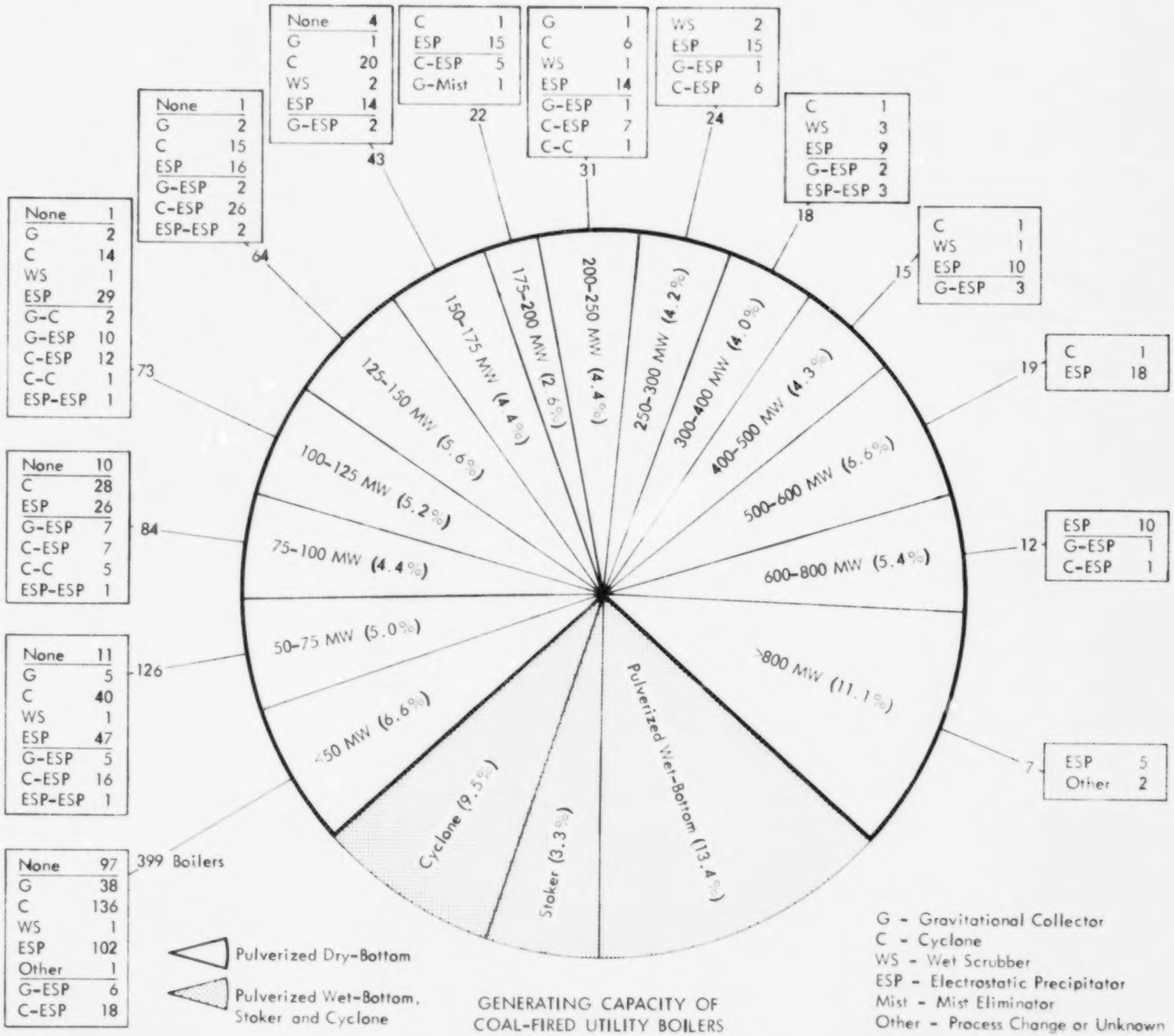


Figure 9. Utility boiler characteristics "tree."[20]

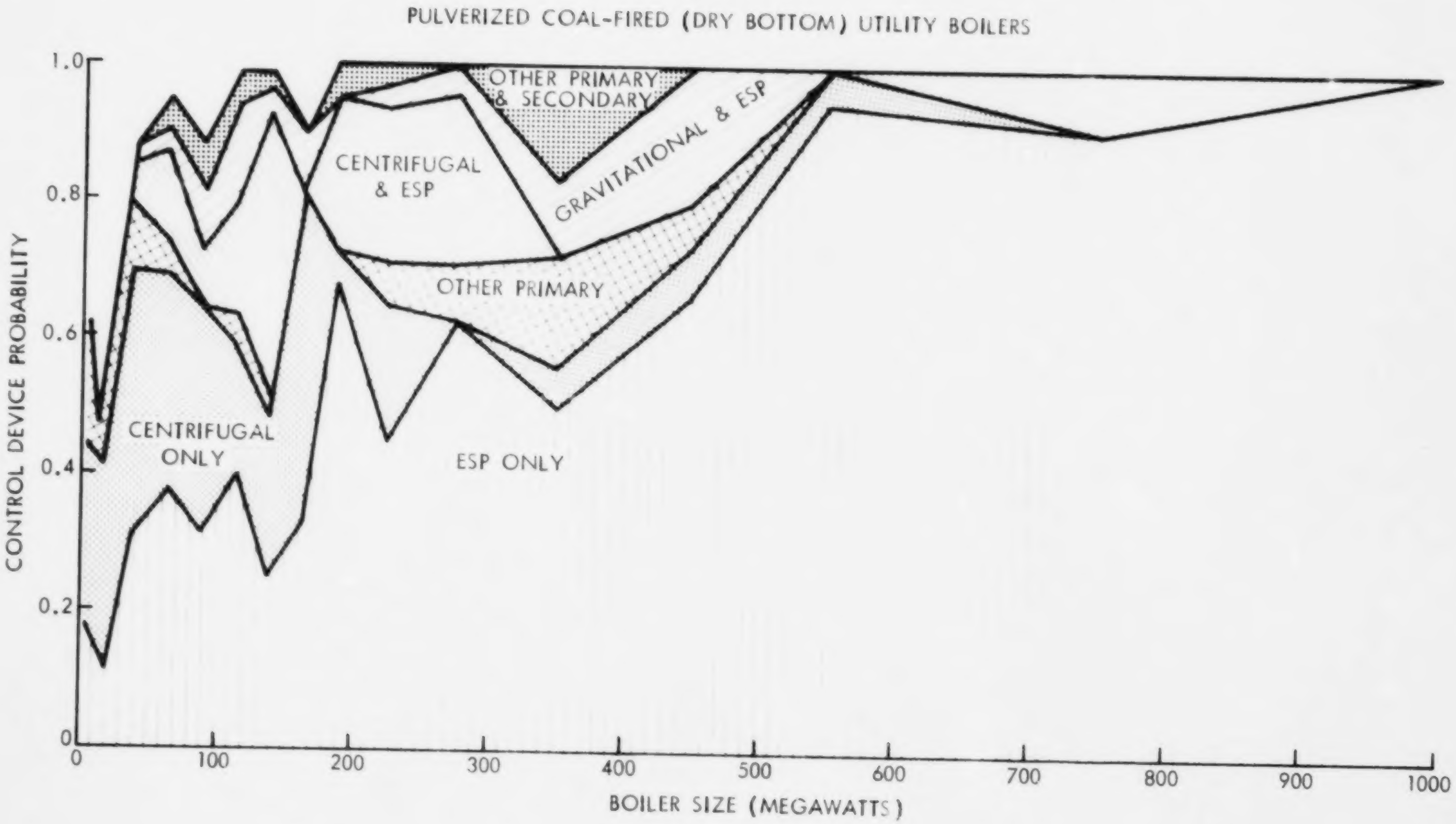


Figure 10. Control devices vs boiler size.20/

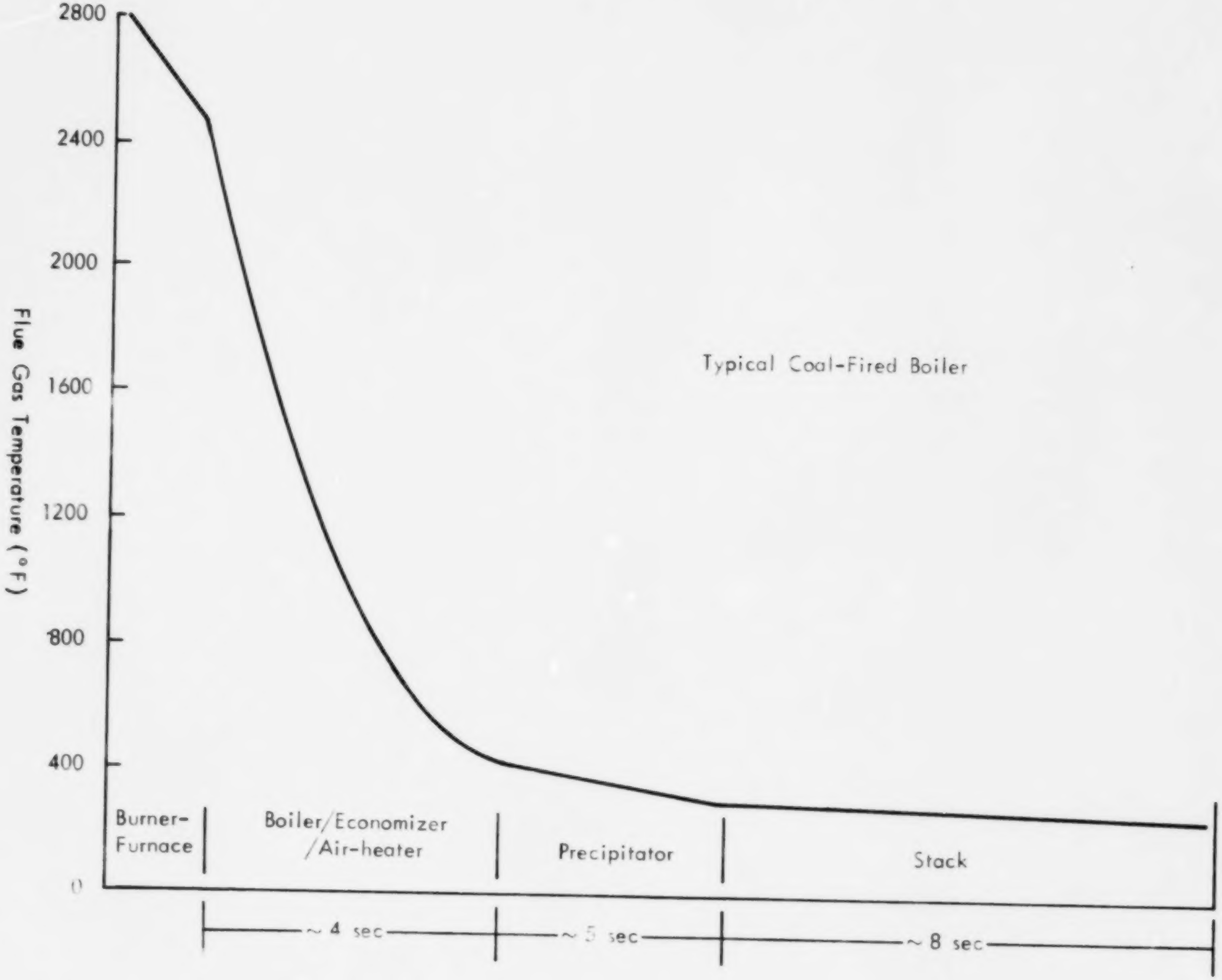


Figure 11. Temperature history of flue gases.

In the practical temperature range of interest (200 to 800°F), hazardous pollutants may exist either in the vaporous state or as one of the following categories of particulates: (a) solid or molten particles, largely inorganic oxides; (b) nucleated material from supersaturated vapors (partial pressure exceeding vapor pressure of condensed phase) in the gradually cooling flue gases; (c) material added to solid or liquid particles by physical or chemical sorption; and (d) condensible material that originates through chemical reaction. The volatility of an individual constituent is a major factor in determining its physical form. In most cases, the more volatile the element, the more likely it will escape as an uncondensed vapor, or as a fine particulate. Most trace metals are released as oxides although some heavy metals such as mercury are so electropositive that they may appear as the free element.

SECTION V

FIELD TESTING PROCEDURES

This section describes (a) the selection of the test boiler, (b) sampling and analysis methods used to measure hazardous emissions and (c) process monitoring procedures. The testing program was designed to yield essential information on the following aspects of individual hazardous pollutants:

1. Mass emission rate.

2. Physical state (including particle size) versus location in flue gas stream.

3. Efficacy of removal by commonly used particulate emission control devices.

4. Distribution among process waste streams (mass balance).

5. Effect of process variations.

TEST FACILITY SELECTION

The following representativeness criteria (as developed in Section III) were used in the selection of the test boiler:

1. Pulverized coal-firing, dry-bottom (representing 73.8% of coal-fired utility boiler generating capacity).

2. Representative megawatt size, i.e., most probable size (~ 122 MW) of pulverized coal-fired utility boilers larger than 50 MW (Figure 7).

3. Available coal from the Appalachian or Interior Eastern source region (accounting for 91% of utility boiler coal consumption).

4. Common particulate emission control device (Figures 9 and 10).

In addition, it was considered highly desirable that extensive data from previous tests be available so that specific sampling requirements could be determined without the necessity of preliminary testing. Finally, the cooperation of plant personnel was considered essential to the success of the program.

Table 10 lists utility boilers in the high density size range (100 to 150 MW) which generally were found to meet the representativeness criteria; however, in some cases preliminary test have may have been lacking and/or utility personnel may not have been favorably disposed to the proposed testing. A 125-MW boiler at TVA's Widows Creek steam-electric generating station was judged to best comply with the selection criteria.

FLUE GAS (MASS-RATE) SAMPLING

The major elements of a flue gas sampling methodology consist of the sampling train design, the selection of test locations, and the detailed sampling procedures. Each of these elements will be discussed below, particularly with regard to special problems which were anticipated in the sampling of hazardous pollutants. A number of comprehensive treatises on sampling methodology[26,27]/ have been written which review general requirements and describe the reference procedures which have been developed.

Sampling Locations

Two general flue gas sampling locations were dictated by the test objectives: (a) control device inlet (400°F); and (b) control device outlet (300°F). The following criteria were used in selecting specific locations:

1. The flow within the duct should be relatively free of mechanical disturbances (indicated by large-scale velocity fluctuations).

2. Adequate space for sampling equipment must be available outside the duct; that is, there should be no physical obstructions within a distance of at least one duct diameter.

3. Standards of safety for the test crew must be met.

Table 10. CANDIDATE TEST FACILITIES (100-150 MW)[a]

Utility	Location	Plant	Previously Tested			NEDS DATA[20]							
			OAP	CSI	Cooperative[b]	Boiler Size (MW)	Control Equipment Type	Control Equipment Eff (%)	Coal Ash Content (%)	Coal Sulfur Content (%)	Firing Type[c]	Desulf System[d]	Coal Source[d]
Cincinnati Gas & Electric	Ohio	W.C. Beckjord			X	105, 136	ESP, C-ESP	95, 96	16.9	2.8	--		A, IE
		Miami Fort			X	143	C-ESP	96	13.5	3.7	--		A, IE
Dayton Power & Light	Ohio	F.M. Tait			X	124	C-ESP	97.5	13.1	1.6	T		A
Detroit Edison	Michigan	St. Clair				146(3)	C-ESP	98.1	12.9	3.0	F		A
Duke Power	So. Carolina	Lee	X			132	G	85	6.8	1.0	--		A, IE
Georgia Power	Georgia	Hammond			X	104(3)	G-ESP	85-98	10.3	2.46	--		IE, A
		Yates			X	116(3), 134(1)	G-ESP	98	10.7	2.31	--		IE, A
Gulf Power	Florida	Lansing Smith				130, 141	ESP	97	--	--	--		IE, A
Illinois Power	Illinois	Wood River	X	X	X	110	C-ESP	99.5	10.6	2.9	--	X	IE
Kansas Power & Light	Kansas	Lawrence	X	X		125	WS	99	12.8	3.8	--	X	IW
Northern Indiana P. S.	Indiana	Mitchell		X		115	ESP	98	9.8	3.07	T or F	1976	IE
Pennsylvania Power	Pennsylvania	Martins Creek			X	138(2)	ESP's	99.8	13.3	3.08	F		A
Potomac Electric	Washington, D.C.	--	X			139	ESP	96	9.5	1.0	T		A
TVA	Alabama	Widows Creek		X		125[f]	M[e]						A

---

a/ Pulverized coal-fired utility boilers.

b/ Known to be cooperative by Control Systems Laboratory (CSL).

c/ From Edison Electric Institute listing:[22] T = tangent; F = front-fired.

d/ From *Air/Water Pollution Report*.

e/ From Keystone Coal Industry Manual: A = Appalachian; IE = Interior Eastern; IW = Interior Western.

f/ Not included in NEDS listing.

Sampling Procedures

Pending the results of current research on the reliability of pollutant source sampling methods as a function of parent gas conditions, it was decided that the flue gas sampling procedures should be patterned after the widely used EPA Standard Methods.28/ This includes the following determinations:

1. Sampling point distribution by Method 1.

2. Preliminary velocity profile by Method 2.

3. Dry carrier gas composition by Method 3.

4. Preliminary moisture content by Method 4.

5. Hazardous pollutant emissions (particulate and vaporous) by Method 5 (modified).

6. SO_2 emissions by Method 6.

7. NO_x emissions by Method 7.

Hazardous Pollutant Sampling Train

A single integrated sampling train, modeled after the Method 5 train, was developed for measurement of mass flow rate of hazardous pollutants. In the absence of the availability of adequately developed sampling trains for hazardous pollutants, an integrated train offered the advantage of physical manageability in typically confined sampling locations. The mass rate train (diagrammed in Figure 12) was designed for efficient collection of a variety of potentially hazardous compounds: trace elements, organics, minor cationic elements, sulfates and nitrates. Collection devices were positioned to minimize interpollutant interferences during subsequent chemical analysis.

Specifically, the sampling train consisted of:

1. A Teflon-lined flexible probe, 12 ft long and heated to stack temperature.

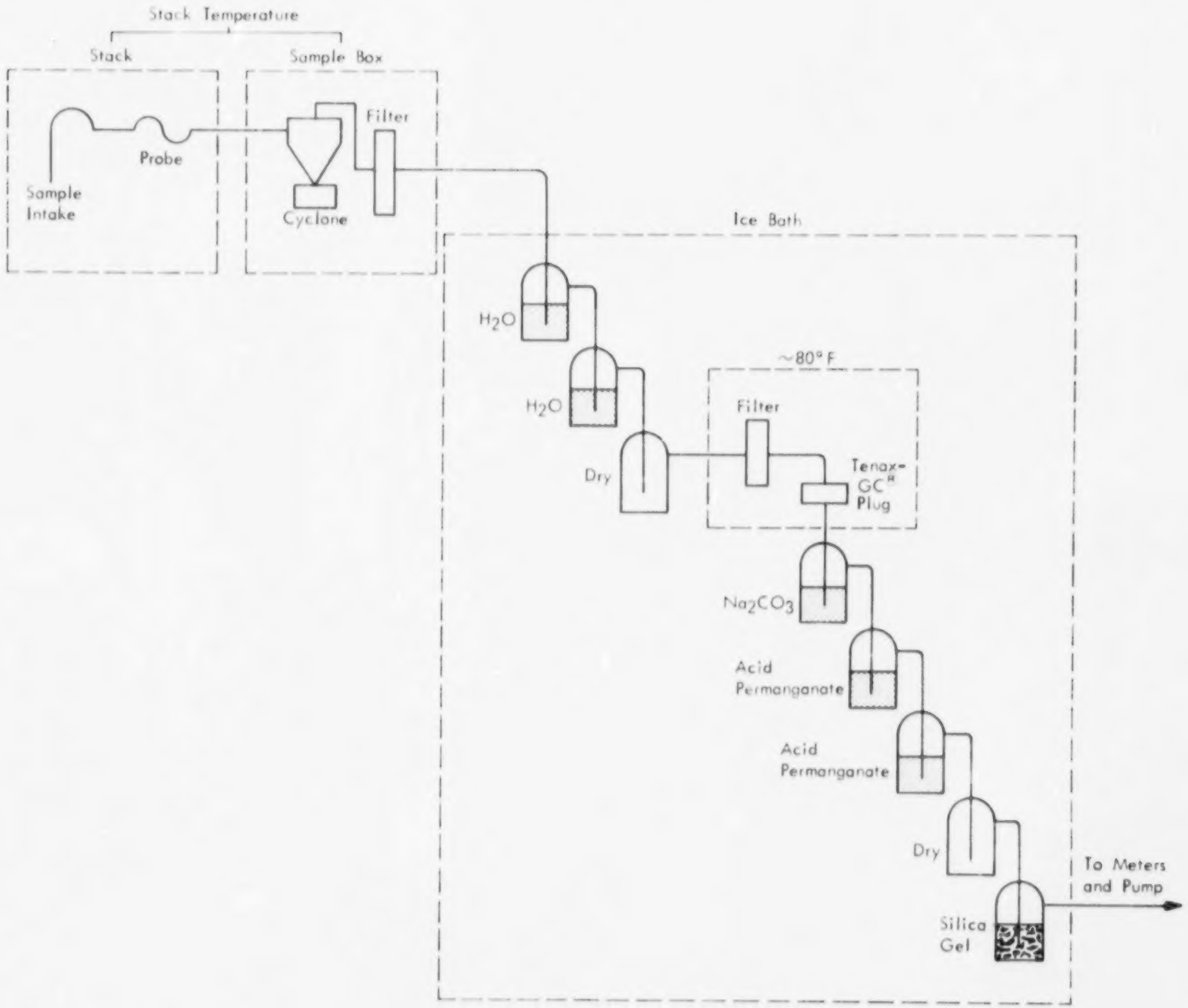

Stack Temperature
Stack
Sample Box
Sample Intake
Probe
Cyclone
Filter
Ice Bath
H_2O
H_2O
Dry
~80° F
Filter
Tenax-GC®
Plug
Na_2CO_3
Acid Permanganate
Acid Permanganate
Dry
Silica Gel
To Meters and Pump

Figure 12. Flue gas sampling train.

2. A quartz-fiber filter, heated to stack temperature (for collection of particulates). A glass cyclone, shown in the diagram (Figure 12), is generally used but was not for this study.

3. Eight impingers in an ice-water bath for collection of condensibles and vaporous species: first two impingers containing water (for removal of condensed water, POM's and PCB's); third impinger, dry (for removal of carry-over from second impinger); fourth impinger, 10% sodium carbonate (for removal of selenium and sulfur dioxide); fifth and sixth impingers, 10% sulfuric acid, 3% permanganate (for removal of inorganic vapors); seventh impinger, dry (for removal of carry-over from sixth impinger); and eighth impinger, silica gel (for removal of residual water vapor).

4. Quartz-fiber filter at approximately 80°F between third and fourth impingers for collection of condensed particulate.

5. Pyrex tube packed with Tenax-GC® for collection of organic vapors (polymeric material used as packing for chromatographic columns).

6. Gas meters and pump as prescribed by EPA Method 5.

The individual components of the specified train were commercially available; however, some modifications were necessary to properly assemble the components.

The procedures used for removing collected samples from the sampling train are detailed in Appendix A.

Particle Size Analysis

Cascade impactors were selected over other in-stack devices for particle sizing because of the following operational advantages:

1. Measurement is effected in the size range of interest for air pollution quantification and control.

2. Aerodynamic impaction is useful over a wide range of particle sizes and concentrations.

3. Aerodynamic size distribution relates directly to environmental effects and controllability.

4. Measurements are not affected by optical or electrical properties of particles.

5. Overall efficiency and fractional efficiency of particulate emission control devices can be measured at the same time.

Brink in-stack cascade impactors were used for particle size analyses at the two flue gas sampling locations. The sizing train (Figure 13) was the basic configuration suggested by the manufacturer of the Brink impactor. The impactors were fitted with tared aluminum foil liners for collection cups.

GROSS COAL AND ASH SAMPLING

To determine the required number of coal and ash samples for accomplishment of test objectives, a simple boiler stream flow model was postulated. The model boiler had one input (coal) stream and three output (ash) streams. True average mass flows of hazardous hazardous pollutant were designated for each stream (Table 11) and the ratio of concentration extremes (i.e., maximum/ minimum) was assumed to be a factor of two for each stream during a given test.

Statistical analysis techniques were applied to determine the number of samples required to estimate the true average mass flow rate of the hazardous pollutant, corresponding to a given tolerance (error), d , and confidence level. The analysis was based on the following assumptions:

1. Measurement and stochastic errors are normally distributed with standard deviations indicated in Table 11.

2. Errors are mutually independent.

The results of the analysis are presented in Table 11.

To achieve acceptable measurement accuracy (i.e., tolerance d = 25% at the 95% confidence level), the model indicated that at least three samples of each coal and ash stream (e.g., furnace bottom ash and fly ash removed by control equipment) were required for each run. Grab samples were sealed in heavy polyethylene bags.

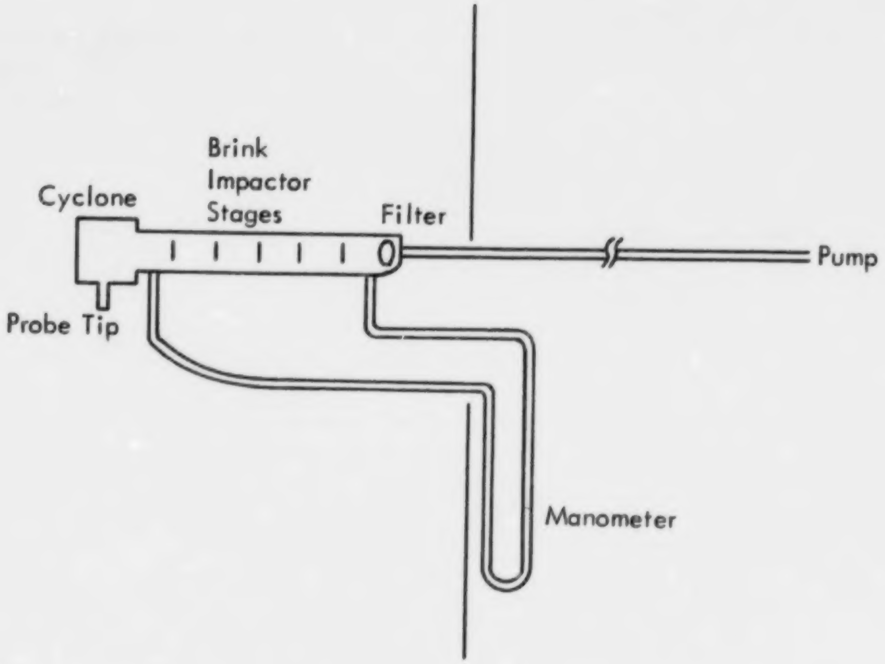

Brink
Impactor
Stages
Cyclone
Filter
Pump
Probe Tip
Manometer

Figure 13. Particle size sampling train.

Table 11. STATISTICAL MODEL FOR DETERMINATION OF SAMPLING FREQUENCY

	True	Relative Standard Deviation (%)				Required Number of Samples Per Run					
						90% Confidence Level			95% Confidence Level		
Stream	Mass Flow	Stream Flow	Pollutant Concentration	Pollutant Flow	Stochastic Error	d=10%	d=20%	d=25%	d=10%	d=20%	d=25%
Input:											
Coal	100	2.5	10.0	10.3	16.7	11	3	2	15	4	3
Output:											
Bottom Ash	20	10.0	10.0	11.4	16.7	12	3	2	16	4	3
Collector Ash	50	10.0	10.0	11.4	16.7	12	3	2	16	4	3
Fly Ash	30	2.5	10.0	10.3	16.7	11	3	2	15	4	3

Note: d = Desired tolerance or an estimate of the range of mass flow rate as a percentage of the average mass flow rate.

INLET AIR SAMPLING

During each run, a conventional high volume filtration unit[29] was used to sample inlet air near the intake to the forced draft fan.

CHEMICAL ANALYSIS OF COLLECTED SAMPLES

This section lists the methods selected for chemical analysis of collected samples. Table 12 presents a summary of the types of samples obtained, the analyses performed on each sample type and the chemical analysis methods. The potentially hazardous pollutants selected for study and the methods that were for chemical analysis of each pollutant are given in Table 13. Figures 14 and 15 indicate the specific analyses performed on discreet samples taken from various components of the hazardous pollutant sampling train and the particle sizing train, respectively.

The procedures used for sample handling, preparation and analysis are described in Appendix A. A review of chemical analysis methods which are applicable to the determination of hazardous constituents in utility boiler flue gases, is presented in Appendix B.

PROCESS MONITORING

The key process operating parameters which affect flue gas temperature and composition (and, presumably, hazardous pollutant characteristics) are listed in Table 14. The test plan required that these quantities be precisely determined and held constant (within normal control limits) during each run. Excess air was measured at the flue gas sampling locations and the other parameters were derived from boiler and generator gauge readings.

For each test, the load factor was maintained near 100%. Previous MRI test data (Figure 16) indicate that particulate emissions are linearly dependent on load factor for loads above 75% of capacity.

Also during each run, boiler heat input was measured to provide the basis for hazardous pollutant emission factors and to check compliance with federal performance standards for utility boilers. Heat input was determined from fuel flowmeters and confirmed (a) by fuel analysis data (see Gross Coal and Ash Sampling and Analysis Section) and measured flue gas characteristics and (b) by a heat and mass balance over the steam generation system.

Table 12. SAMPLES AND ANALYSES

Sample type	Analyses	Analytical methods
Coal	Combustion properties Composition Hazardous pollutants	Proximate analysis[a] Ultimate analysis[a] Table 13
Ash (bottom ash, superheater ash, dust collector ash)	Combustion properties Hazardous pollutants	Proximate analysis Table 13
Flue gas		
Particulates and vapors	Hazardous pollutants Total particulates	Table 13 Gravimetry
Particle size	Hazardous pollutants Total particulates	Table 13 Gravimetry
Criteria gases	Sulfur dioxide Nitrogen oxides	EPA Method 6 EPA Method 7
Carrier gases	Oxygen Carbon dioxide Carbon monoxide Nitrogen	Orsat (EPA Method 3)
Inlet air	Total suspended particulates	Gravimetry

---

[a] American Society for Testing and Materials (ASTM) Method D271-70.

Table 13. CHEMICAL ANALYSIS METHODS

Pollutant	Methods of analysis[a]
Trace elements (cations)	
Antimony	1[b]
Arsenic	1[b]
Barium	1
Beryllium	1
Cadmium	2
Chromium	1
Cobalt	1
Copper	1
Lead	2
Manganese	1
Mercury	2[c]
Nickel	1
Selenium	1[b]
Tellurium	1
Tin	2
Titanium	1
Vanadium	1
Zinc	1
Minor elements (cations)	
Calcium	1
Iron	1
Anions	
Chloride	3
Fluoride	4
Nitrate	7
Sulfate	8
Organics	
POM	6
PCB	5

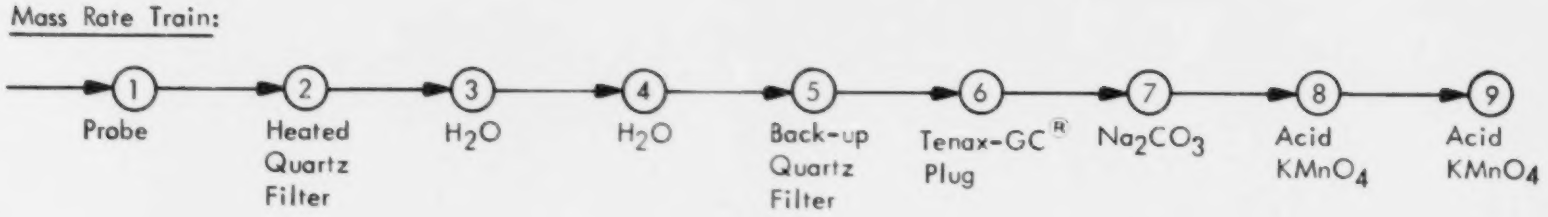
---

[a] The methods of analysis are as follows:

(1) Atomic Absorption Spectrometry (AAS), conventional flame methods;
(2) AAS, micro flameless methods;
(3) $AgNO_3$ titration, electrochemical (EC) detection;
(4) EC, fluorine selective electrode;
(5) Gas chromatography (GC), electron capture detection;
(6) GC, flame ionization detection;
(7) Spectrophotometric, phenol disulfonic acid complex; and
(8) Barium perchlorate titration.

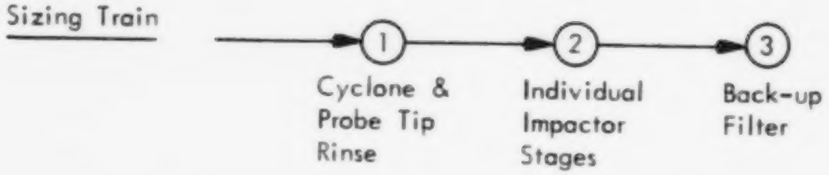
[b] AAS, hydride generation methods.

[c] AAS, cold vapor method.


Mass Rate Train:
1
Probe
2
Heated Quartz Filter
3
H_2O
4
H_2O
5
Back-up Quartz Filter
6
Tenax-GC® Plug
7
Na_2CO_3
8
Acid $KMnO_4$
9
Acid $KMnO_4$

Sample Analysis	1	2	3	4	5	6	7	8	9
Elemental	●	●							
Sb, As, Hg, Se	●	●					●	●	●
Chloride, Fluoride	●	●	●						
Sulfate, Nitrate	●	●							
POM, PCB	●	●	●	●	●	●			
Particulates	●	●	●	●					

Figure 14. Analyses for flue gas sampling train.


Sizing Train
1
2
3
Cyclone & Probe Tip Rinse
Individual Impactor Stages
Back-up Filter

Sample Analysis	1	2	3
Metals	●	●	●
Particulates	●	●	●

Figure 15. Analyses for particle size sampling train.

Table 14. OPERATING VARIABLES

Variable	Practical Range	Primary Effects on Flue Gas
Load Factor[a]	50 to 100%	. Flue gas flow rate . Flue gas temperature profile . Flue gas composition . Combustion efficiency
Excess Air	10 to 35%	. Flue gas composition . Combustion efficiency . Flue gas flow rate
Soot Blowing	. Time between soot blowing operations	. Flue gas composition (particulate loading)

---

[a] Percentage of rated boiler capacity at any point in time.

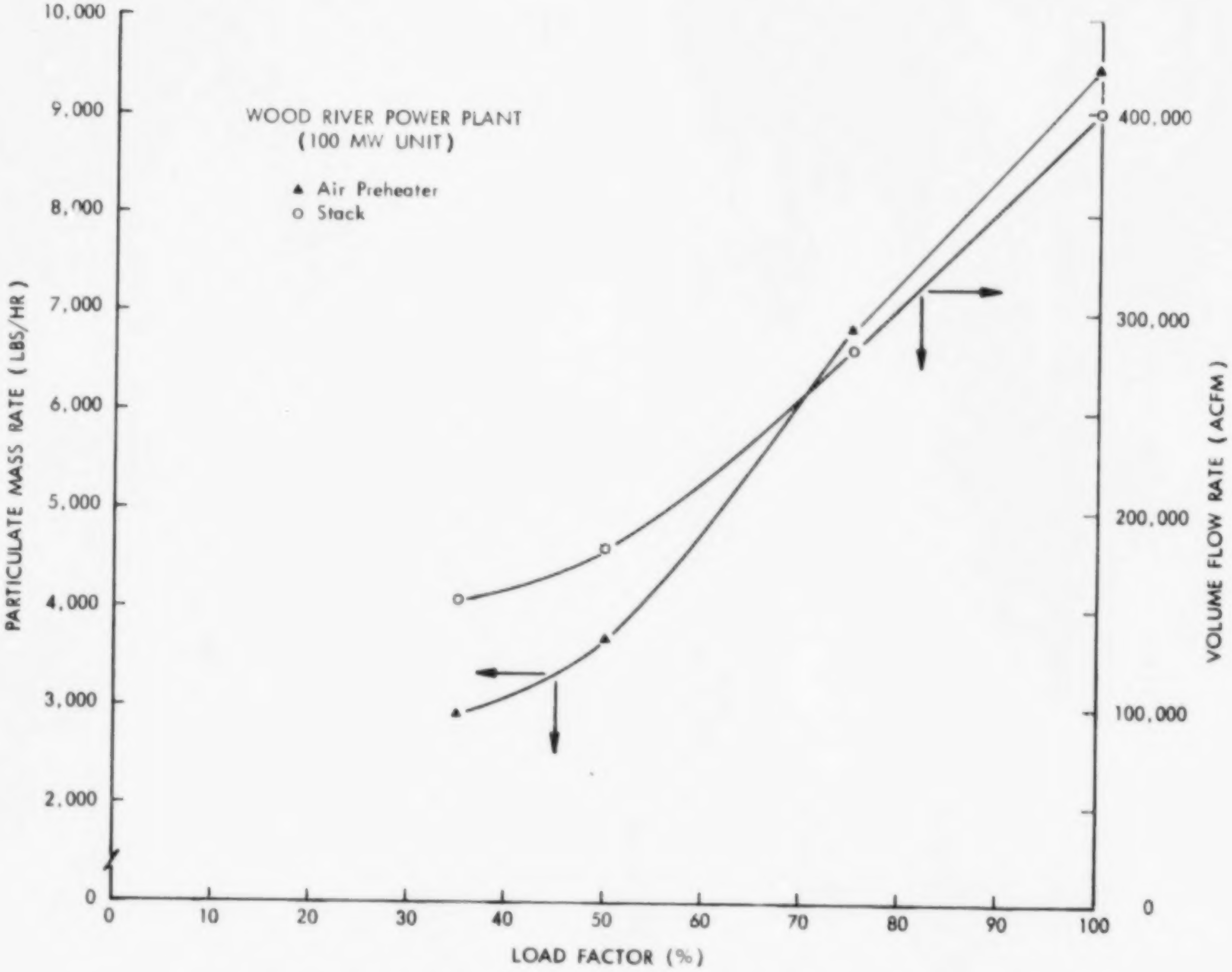
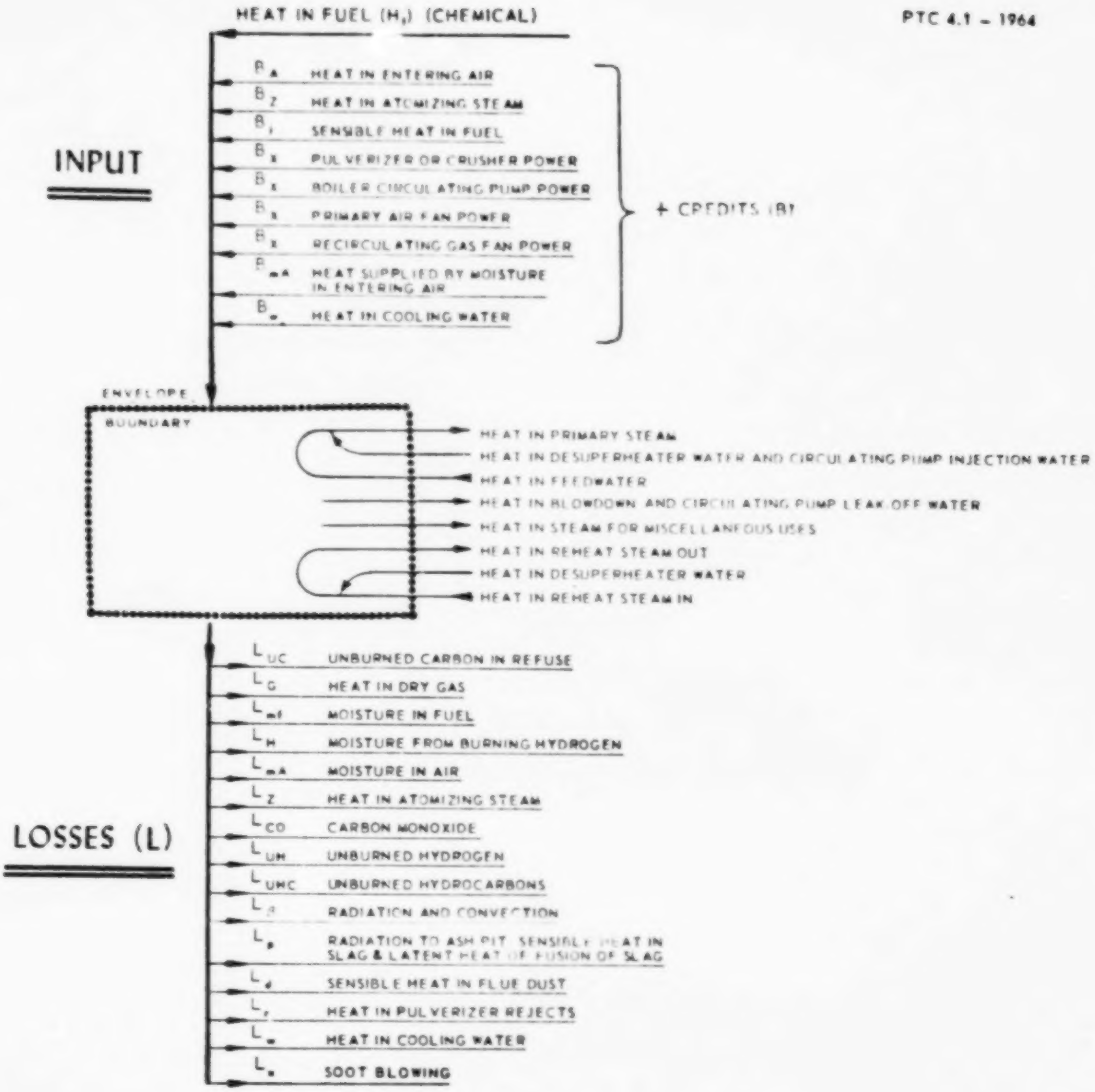


Figure 16. Dependence of emissions on load factor.

For the heat and mass balances, the mass flow rates of major input/output process streams (Figure 2) were measured during each run. Data for these determinations included: (a) continuous readings from boiler control room meters, recorded continuously or periodically; (b) scale dump counts; and (c) flue gas measurements.

Boiler steam efficiency (Figure 17) was determined for each run using the abbreviated heat loss method specified in American Society of Mechanical Engineers (ASME) Performance Test Code 4.1 (1964). The calculation method is presented in Appendix C.


HEAT IN FUEL (H_f) (CHEMICAL)
PTC 4.1 – 1964
INPUT
B_A HEAT IN ENTERING AIR
B_Z HEAT IN ATOMIZING STEAM
B_f SENSIBLE HEAT IN FUEL
B_x PULVERIZER OR CRUSHER POWER
B_x BOILER CIRCULATING PUMP POWER
B_x PRIMARY AIR FAN POWER
B_x RECIRCULATING GAS FAN POWER
B_{mA} HEAT SUPPLIED BY MOISTURE IN ENTERING AIR
B_w HEAT IN COOLING WATER
+ CREDITS (B)
ENVELOPE BOUNDARY
HEAT IN PRIMARY STEAM
HEAT IN DESUPERHEATER WATER AND CIRCULATING PUMP INJECTION WATER
HEAT IN FEEDWATER
HEAT IN BLOWDOWN AND CIRCULATING PUMP LEAK-OFF WATER
HEAT IN STEAM FOR MISCELLANEOUS USES
HEAT IN REHEAT STEAM OUT
HEAT IN DESUPERHEATER WATER
HEAT IN REHEAT STEAM IN
LOSSES (L)
L_{UC} UNBURNED CARBON IN REFUSE
L_G HEAT IN DRY GAS
L_{mf} MOISTURE IN FUEL
L_H MOISTURE FROM BURNING HYDROGEN
L_{mA} MOISTURE IN AIR
L_Z HEAT IN ATOMIZING STEAM
L_{CO} CARBON MONOXIDE
L_{UH} UNBURNED HYDROGEN
L_{UHC} UNBURNED HYDROCARBONS
L_β RADIATION AND CONVECTION
L_p RADIATION TO ASH PIT, SENSIBLE HEAT IN SLAG & LATENT HEAT OF FUSION OF SLAG
L_d SENSIBLE HEAT IN FLUE DUST
L_r HEAT IN PULVERIZER REJECTS
L_w HEAT IN COOLING WATER
L_s SOOT BLOWING

OUTPUT = INPUT − LOSSES

DEFINITION: EFFICIENCY (PERCENT) = $\eta_g (\%) = \frac{\text{OUTPUT}}{\text{INPUT}} \times 100 = \frac{\text{INPUT} - L}{H_f + B} \times 100$

HEAT BALANCE: $H_f + B = \text{OUTPUT} + L$ OR $\eta_g (\%) = \left[1 - \frac{L}{H_f + B}\right] \times 100$

Figure 17. Heat balance of steam generator.

SECTION VI

TEST FACILITY AND SAMPLING PROGRAM

TEST FACILITY

Unit 5 at the Tennessee Valley Authority Widows Creek steam electric power plant was selected for the testing program. The Widows Creek six-unit installation is located on the west shore of Guntersville Lake (Tennessee River), 5 miles southwest of Bridgeport, Alabama. Unit 5 was put into commercial operation in May 1954.

The major design features of Widows Creek Unit 5 are listed in Table 15. An elevation view of this boiler is given in Figure 18.

Widows Creek Unit 5 is representative of the current population of coal-fired utility boilers and meets the following criteria established for the test facility:

- Pulverized coal firing; dry-bottom furnace.
- 125 MW generating capacity.
- Utilizes coal from Appalachian sources.
- Equipped with common particulate emission control device, i.e., mechanical fly ash collector.

A simplified design drawing for Unit 5 is shown in Figure 19. Pulverized coal is pneumatically conveyed from four pulverizers to 16 forced-draft burners, eight in each half of the divided furnace. Combustion gases leaving either side of the boiler pass vertically through a Ljungstrom-type air preheater and then turn abruptly into the mechanical fly ash collectors.

Table 15. WIDOWS CREEK UNIT 5 DESIGN DATA

Power capability: 125 MW

Boiler type: Single pass, divided furnace, water wall, dry bottom, radiant, reheat boiler

Boiler efficiency: 88.45% at 112.5 MW

Firing method: Horizontal firing of pulverized coal

Fly ash collector: Two four-bank multiclone units

Bottom ash system: V-type furnace bottom hoppers with water sluice

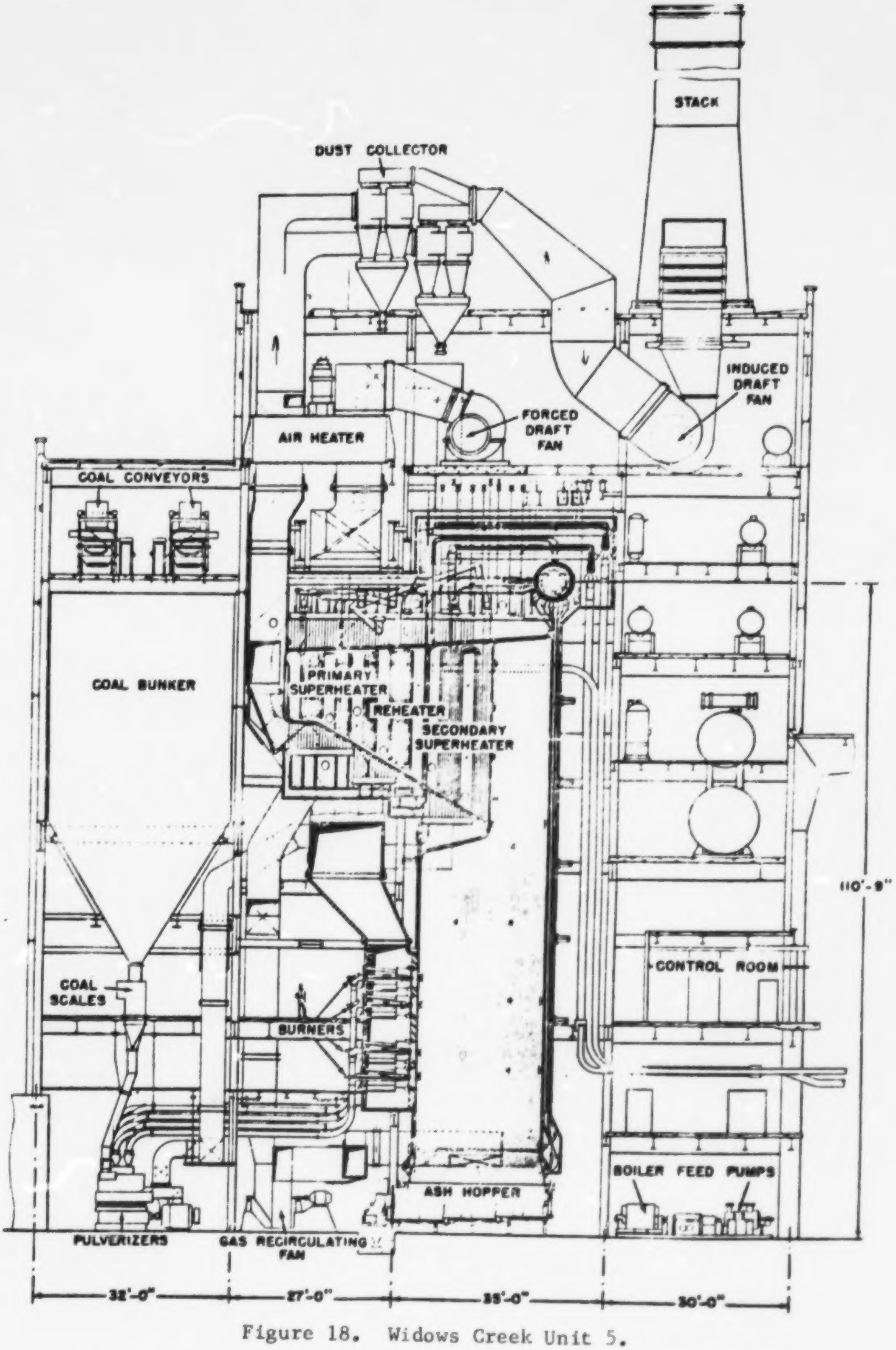

STACK
DUST COLLECTOR
INDUCED DRAFT FAN
FORCED DRAFT FAN
AIR HEATER
COAL CONVEYORS
COAL BUNKER
PRIMARY SUPERHEATER
REHEATER
SECONDARY SUPERHEATER
110'-9"
CONTROL ROOM
COAL SCALES
BURNERS
ASH HOPPER
BOILER FEED PUMPS
PULVERIZERS
GAS RECIRCULATING FAN
32'-0"
27'-0"
35'-0"
30'-0"

Figure 18. Widows Creek Unit 5.

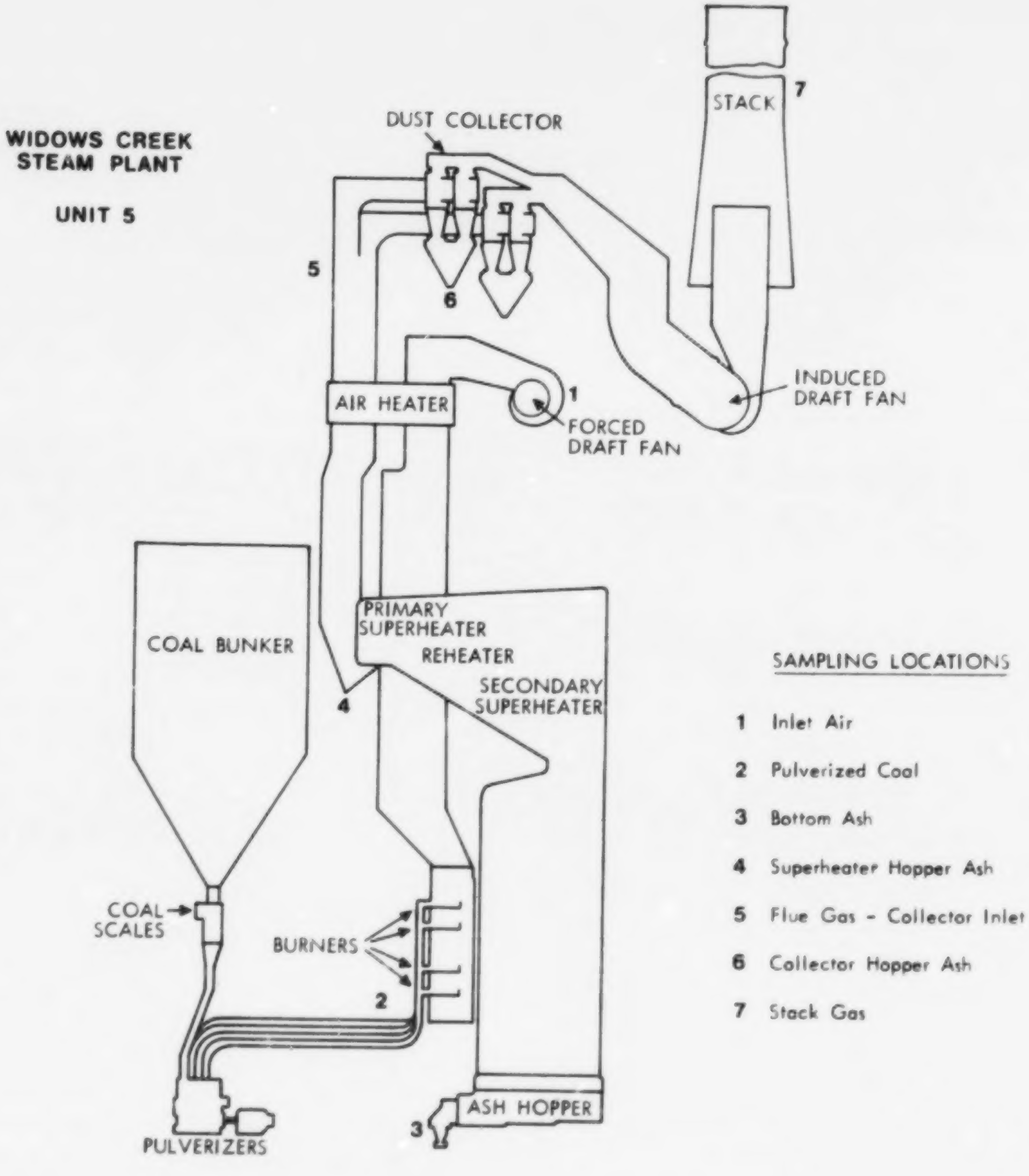

WIDOWS CREEK
STEAM PLANT
UNIT 5
DUST COLLECTOR
STACK
7
5
6
1
AIR HEATER
FORCED DRAFT FAN
INDUCED DRAFT FAN
COAL BUNKER
PRIMARY SUPERHEATER
REHEATER
SECONDARY SUPERHEATER
4
COAL SCALES
BURNERS
2
PULVERIZERS
3
ASH HOPPER
SAMPLING LOCATIONS
1 Inlet Air
2 Pulverized Coal
3 Bottom Ash
4 Superheater Hopper Ash
5 Flue Gas - Collector Inlet
6 Collector Hopper Ash
7 Stack Gas

Figure 19. Simplified diagram of test facility.

Flue gases from each collector are drawn down to the induced draft fan and then are discharged through breeching to the 150-ft stack and finally into the atmosphere. Figure 19 indicates the locations for sampling inlet air, coal, flue gas and ash.

This unit presented a number of sampling problems which are typical of utility boilers. These are listed below in order of sampling location (Figure 19):

- Station 3: Bottom ash (in sluice water) could be sampled from the ash hopper, but it was not possible to estimate directly the total mass flow rate of bottom ash.

- Stations 4 and 6: Fly ash could be sampled from the superheater and mechanical collector hoppers, but it was not possible to estimate directly the total mass flow rate of these ash streams.

- Station 5: The number of equivalent duct diameters between the Ljungstrom air heater and the bend to the dust collectors was insufficient to assure a sampling location with rectilinear flow and without significant turbulent fluctuations. Also, at this station, there was insufficient space between the accessible sides of the ducting and the dust collector hoppers (and bracing) to permit use of a rigid probe.

- Station 7: The ducting between the dust collector outlets and the inlet to the induced draft fan followed a tortuous flow path, which was judged to be unacceptable for sampling. This made it necessary to sample on the stack, which, prior to this test program, was not equipped with sampling ports or platforms.

The most serious of these sampling problems were those produced by the flow obstructions upstream of Station 5. However, the flow disturbances caused by the fins of the air heater and the transition from half-circular to rectangular cross section at the air heater outlet, were judged to be much less disruptive than those caused by other types of duct configurations. The potential impact of flow disturbances on representative sampling at Station 5 was minimized by increasing the number of sampling points. In addition, to overcome external space limitations, a flexible, heated probe was designed and fabricated for use at this station.

At the stack (Station 7) the number of sampling points was also increased so that distance of the sampling cross section above the diameter reduction (at the base of the stack) could be held to a minimum (approximately two stack diameters). A painters platform hung from the top of the stack was used to support men and equipment at this station.

The sampling problems encountered at Widows Creek were judged to be about average for a utility boiler. On the positive side, Station 5 was conveniently located on the roof of the plant, and there were easily accessible ports for coal and ash sampling.

SAMPLING PROGRAM

Table 16 gives the composition of the MRI field crew who carried out the sampling program at Widows Creek. Because of the split-duct design of the flue gas flow system, duplicate sampling teams were required at the two collector inlet sampling locations (Stations 5A and 5B).

The Widows Creek sampling program was conducted during the period 15-24 August of 1974. Figures 20 through 22 summarize the main sampling program (Runs 2 through 4). For each sampling station, the times and duration of sampling and the number of samples are specified.

Flue Gas Sampling

Hazardous Pollutants - Flue gas sampling to determine mass flow rate of hazardous pollutants (particulates and vapors) and particle size distribution was performed at the inlet and outlet to the dust collector (Stations 5 and 7, respectively). In addition, at the outlet of the dust collector, flue gases were sampled for sulfur dioxide, nitrogen oxides and bulk carrier gas composition.

Figure 23 shows the ductwork configuration and the distribution of sampling points at either of the dust collector inlet sampling stations. During a run, each of the 48 points was sampled for 4 min. Both inlet stations were sampled simultaneously with separate sampling trains.

Table 16. MRI FIELD SAMPLING CREW

Responsibility	Sampling station	Number of personnel
Crew chief	-	1
Flue gas sampling		
Mass train console	5A	1
	5B	1
	7	1
Mass train probe	5A	1
	5B	1
	7	1
Size train	5A	1
	5B	1
	7	1
Gas trains	7	1
Coal/ash sampling[a]	2, 4, 6	2
Inlet air sampling	1	1
Process monitoring		1
Field laboratory		
Mass train		2
Size train		1
Total		16

---

[a] Bottom ash samples were collected by Widows Creek plant personnel.

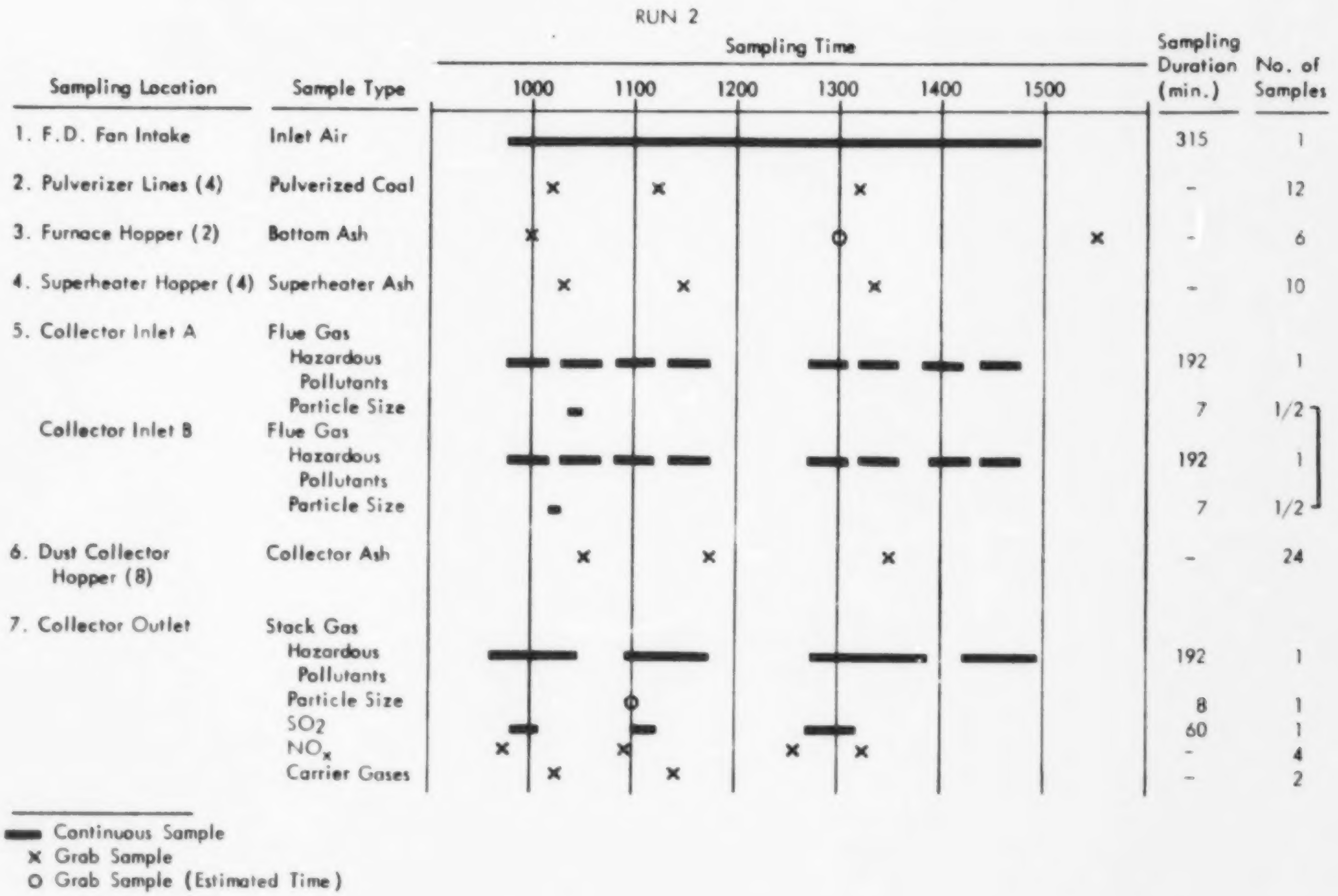


Figure 20. Sampling program - Run 2

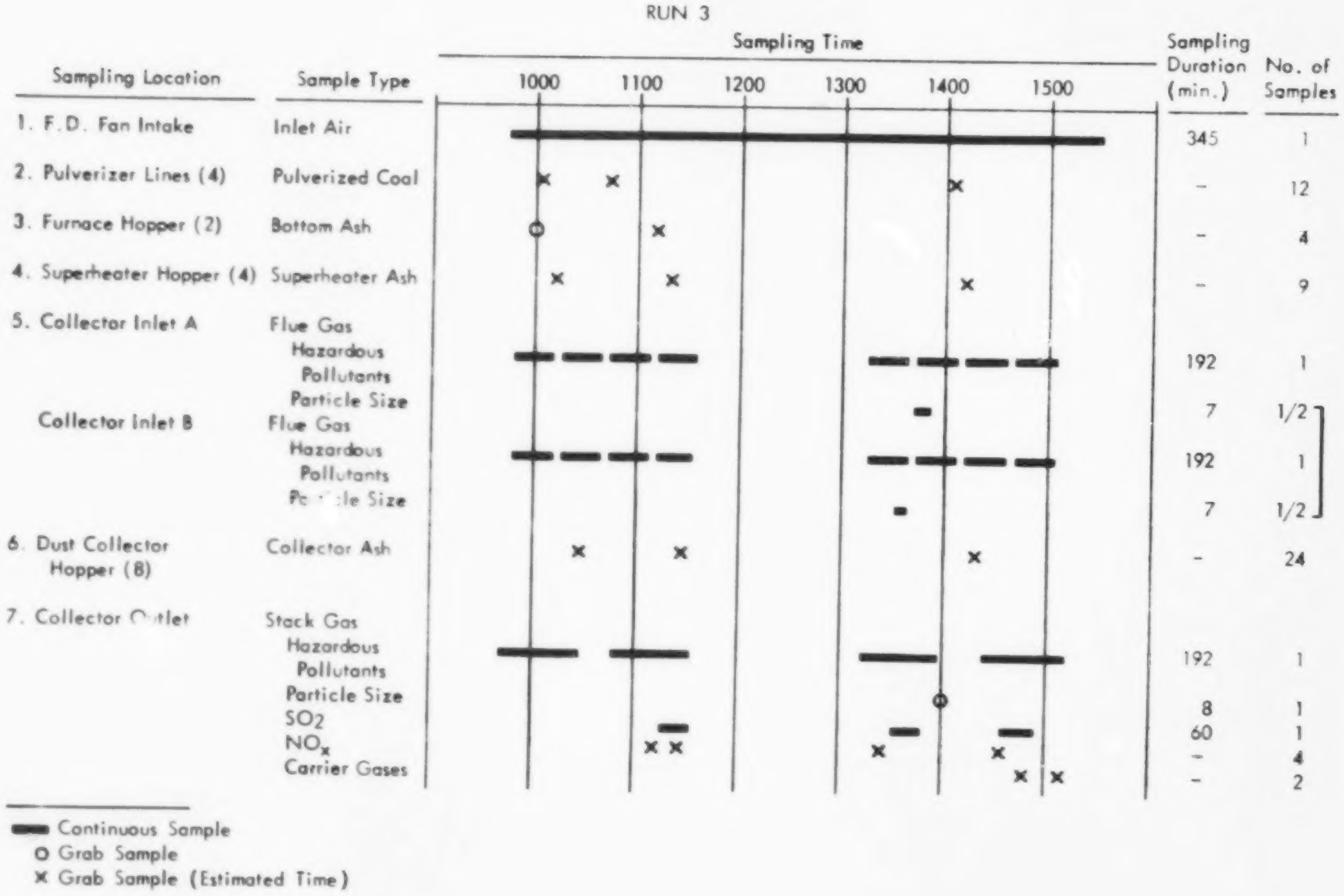


Figure 21. Sampling program - Run 3.

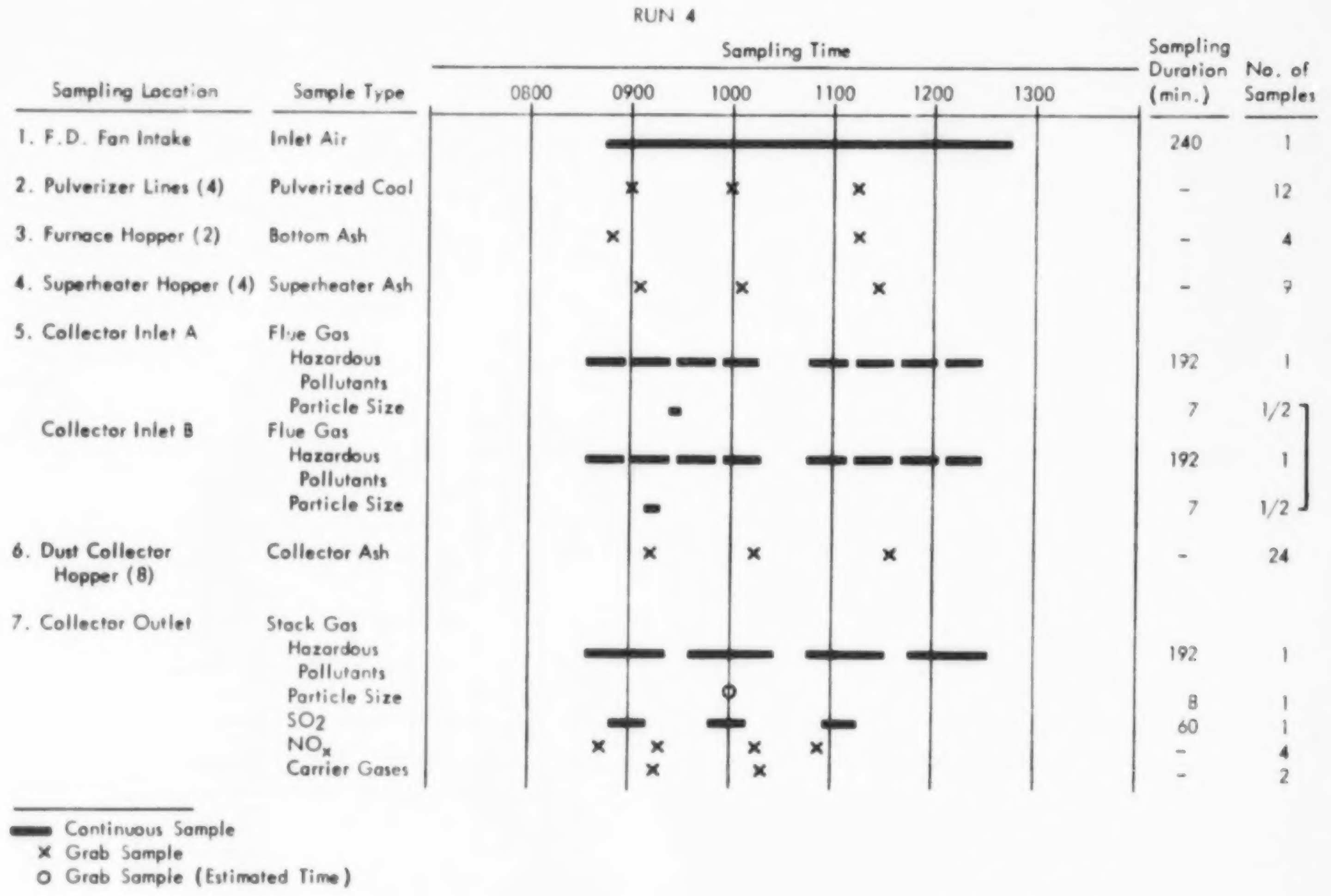


Figure 22. Sampling program - Run 4.

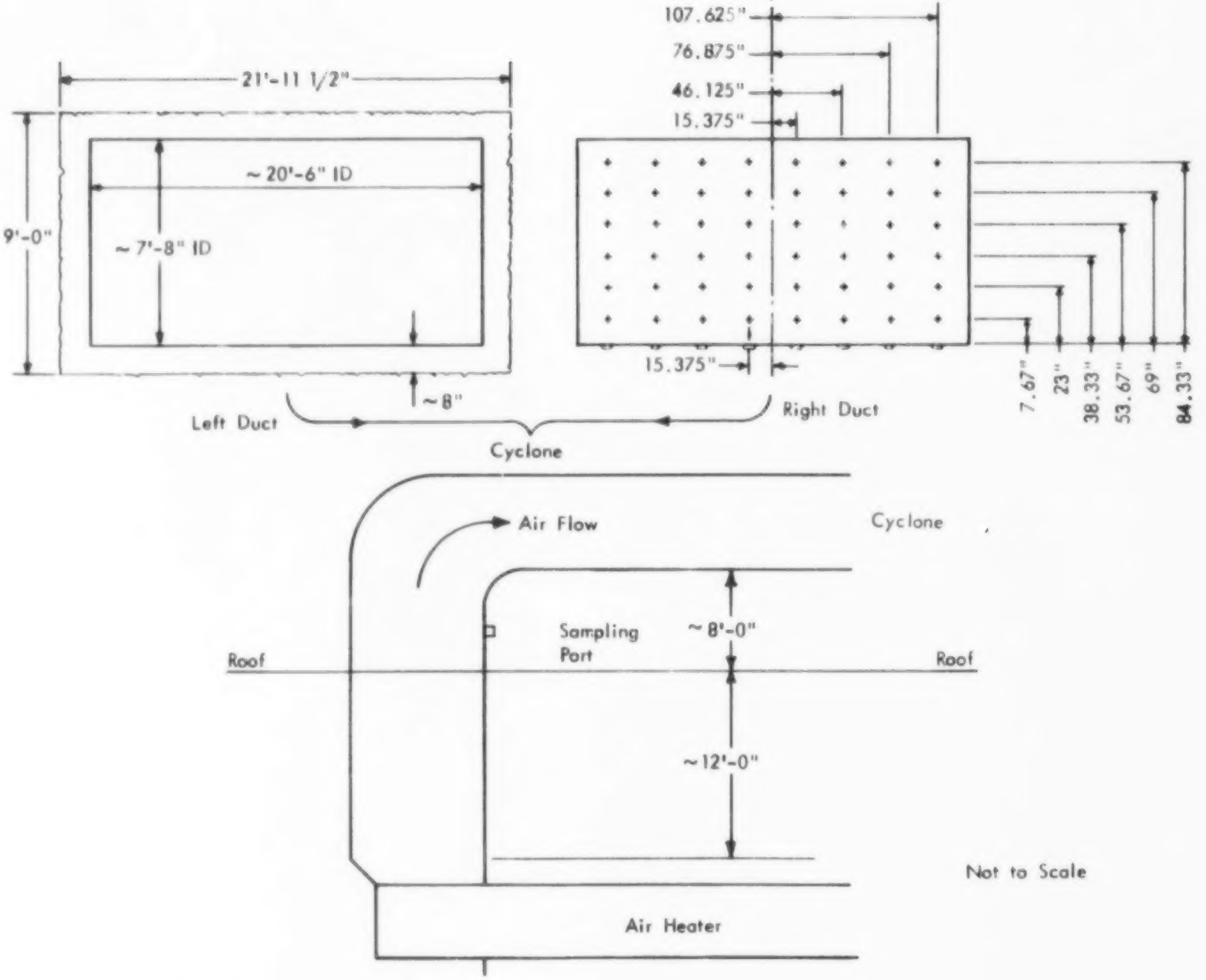

21'-11 1/2"
9'-0"
~20'-6" ID
~7'-8" ID
~8"
107.625"
76.875"
46.125"
15.375"
15.375"
7.67"
23"
38.33"
53.67"
69"
84.33"
Left Duct
Right Duct
Cyclone
Air Flow
Cyclone
Sampling Port
~8'-0"
Roof
Roof
~12'-0"
Not to Scale
Air Heater

Figure 23. Collector inlet duct configuration.

Figure 24 shows the ductwork configuration and the sampling traverses for the collector outlet sampling location, i.e., the stack. Twenty-four sampling points were distributed along each traverse with spacing as specified by EPA Method 1. Each of the 48 points was sampled for 4 min.

During each run, the inlet and outlet locations were sampled nearly simultaneously (Figures 20 through 22). The duration of sampling and the dry gas volume sampled at each station exceeded the minimums (i.e., 2 hr and 60 cu ft, respectively) specified for the performance testing of utility boilers.28/

Particle Sizing - During each run, two particle size samples were obtained, one each at the collector inlet and outlet sampling stations. Each of the two inlet ducts was sampled (with the same train) for a period of 7 min to obtain a single composite sample; samples were drawn from one point in each duct, about 24 in. from the interior wall. The stack was sampled for 8 min at one point about 24 in. from the interior wall. Prior to each sizing test, the Brink unit was heated in the stack for a period of 30 min to 1 hr to establish thermal equilibrium.

SO_2, NO_x, and Carrier Gases - During each run, gas sampling was distributed over the time required for particulate sampling. A 1-hr SO_2 sample was obtained by sampling for three separate periods of at least 15 min. Also, four grab samples of NO_x and two grab samples of dry carrier gases were obtained. Samples were drawn from points in the flow about 24 in. from the interior wall of the stack.

Coal/Ash Sampling

Based on statistical analysis of a boiler stream flow model (Section IV), it was determined that at least three representative samples of pulverized coal and each ash stream should be taken during each run in order to achieve acceptable measurement accuracy (i.e., tolerance of 25% at the 95% confidence level). A representative grab sample of coal or ash consisted of portions removed from each segment of a divided flow stream, i.e., from the four pulverized coal lines, two bottom ash hoppers, two superheater hoppers, and eight dust collector hoppers.

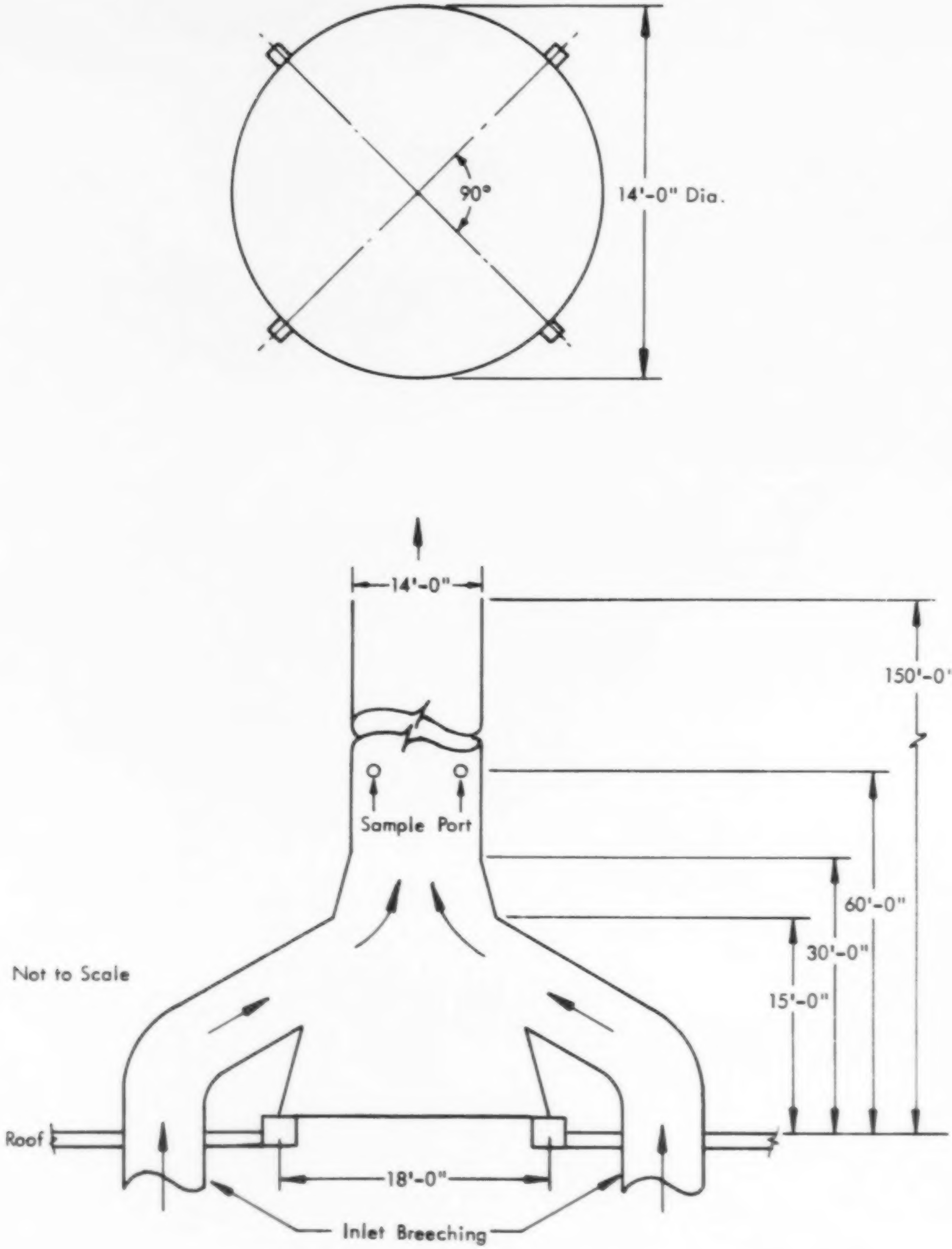

90°
14'-0" Dia.
14'-0"
150'-0"
Sample Port
60'-0"
30'-0"
15'-0"
Not to Scale
Roof
18'-0"
Inlet Breeching

Figure 24. Stack configuration.

Inlet Air Sampling

During each run, inlet air was sampled near the intake to the forced draft fan.

SECTION VII

ANALYTICAL RESULTS AND QUALITY ASSURANCE

This section presents the results of the quantitative analysis of samples obtained in the Widows Creek sampling program. Reporting of results, i.e., mass or concentration of constituents found, is done without direct reference to sampling parameters. However, inferences are made about the collection efficiency of the sampling train. Problems in carrying out the analytical techniques are also discussed along with corrective measures that were taken. Finally, the results of experiments to determine the quality (precision and accuracy) of the analytical results are presented.

ANALYTICAL RESULTS

The analytical results obtained for the various samples collected at Widows Creek are discussed in the following order: (a) coal and ash samples; and (b) flue gas samples.

Coal and Ash Samples

Table 17 lists the results obtained for the hazardous pollutant analyses of coal, bottom ash, superheater ash, inlet fly ash, dust collector ash, and outlet fly ash. The inlet and outlet fly ash results are discussed in more detail in the next section. "Less than (<)" numbers indicated in this table are based on the concentrations required to produce a signal that is twice the noise level.

The values reported for each of the hazardous pollutants appear to have internal consistency. The relative magnitude of the value for coal tends to be reflected in the corresponding ash values. Also, values for a given pollutant are consistent over the three runs.

Table 17. POLLUTANT CONCENTRATION (ppm)[a/] IN COAL, ASH, AND FLUE GAS STREAMS

Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Dust collector ash	Outlet fly ash
Trace elements (cations)							
Antimony	2	< 1.3	1.3	0.31	0.55	b/	1.54
	3	0.7	1.4	1.3	< 1.0	1.4	1.36
	4	< 1.2	1.3	1.1	< 1.3	0.32	1.5
	Avg.	< 1.1	1.3	0.90	< 0.95	< 0.9	1.5
Arsenic	2	13.0	5.6	12.1	8.2	b/	7.4
	3	13.5	7.6	3.2	8.1	b/	5.5
	4	16.3	4.2	5.7	8.8	b/	12.0
	Avg.	14.3	5.8	7.0	8.4	b/	8.3
Barium	2	< 167	905	1,119	1,054	1,213	1,028
	3	< 173	844	592	604	916	1,262
	4	< 165	444	715	986	1,367	931
	Avg.	< 168	731	809	881	1,165	1,074
Beryllium	2	1.6	8.0	6.4	8.2	7.2	10.0
	3	1.5	7.4	5.6	7.7	6.8	8.5
	4	1.4	6.5	6.2	8.2	9.7	9.5
	Avg.	1.5	7.3	6.1	8.0	7.9	9.3
Cadmium	2	1.25	0.50	1.46	4.42	2.89	6.29
	3	0.31	2.01	1.35	4.18	1.14	3.88
	4.	1.40	0.74	1.98	10.73	2.00	14.09
	Avg.	0.99	1.08	1.60	6.44	2.01	8.09
Chromium	2	24	125	109	296	133	316
	3	24	132	105	168	191	170
	4	23	116	130	153	128	174
	Avg.	24	124	115	206	151	220

Table 17. (Continued)

Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Dust collector ash	Outlet fly ash
Cobalt	2	1.84	5.74	5.86	7.09	10.5	3.61
	3	1.51	1.95	4.45	6.49	6.87	2.78
	4	0.99	3.20	3.93	4.36	6.41	4.68
	Avg.	1.45	3.63	4.75	5.98	7.93	3.69
Copper	2	10	51	54	75	59	81
	3	12	48	46	65	74	70
	4	9	45	45	64	39	72
	Avg.	10	48	48	68	57	74
Lead	2	3.68	6.94	11.9	21.8	21.7	18.7
	3	2.26	12.3	10.4	26.1	11.6	29.9
	4	5.23	5.07	9.41	48.2	11.5	61.2
	Avg.	3.72	8.10	10.6	32.0	14.9	36.6
Manganese	2	24	125	217	153	169	164
	3	30	377	265	222	287	154
	4	51	184	326	371	268	285
	Avg.	35	229	269	249	241	201
Mercury	2	1.88	< 0.541	< 0.58	16.7	< 1.21	23.3
	3	1.91	< 0.489	6.90	23.8	< 1.17	2.2
	4	1.93	< 0.502	46.4	18.3	< 1.17	25.4
	Avg.	1.91	< 0.51	< 18.0	20.0	< 1.18	17.0
Nickel	2	18	45	108	178	88	206
	3	16	84	94	128	98	86
	4	12	58	102	97	60	86
	Avg.	15	62	101	134	82	126

Table 17. (Continued)

Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Dust collector ash	Outlet fly ash
Selenium	2	< 6.1	< 5.5	< 6.2	27.9	b/	< 18.9
	3	< 6.1	< 5.9	< 5.7	24.1	b/	< 13.1
	4	6.0	< 5.4	< 5.5	27.5	< 12.5	18.2
	Avg.	< 6.1	< 5.6	< 5.8	26.5	< 12.5	< 16.7
Tellurium	2	< 30	62	30	31	30	< 35
	3	< 30	41	< 27	< 30	31	35
	4	< 30	26	< 27	< 30	28	29
	Avg.	< 30	43	< 28	< 30	30	< 33
Tin	2	1.73	2.83	2.11	3.04	1.74	1.69
	3	1.70	1.81	1.59	3.31	3.48	2.38
	4	1.65	1.45	2.08	2.07	3.45	1.69
	Avg.	1.69	2.03	1.93	2.81	2.89	1.92
Titanium	2	1,090	6,900	5,430	6,420	5,150	6,840
	3	833	5,520	5,480	6,990	6,260	7,410
	4	758	6,010	5,200	5,930	3,940	6,400
	Avg.	895	6,150	5,370	6,450	5,120	6,890
Vanadium	2	61	272	229	308	275	359
	3	61	419	215	238	190	262
	4	64	369	342	478	240	623
	Avg.	62	353	262	341	235	415
Zinc	2	36	68	133	163	154	212
	3	17	275	110	201	131	150
	4	111	107	186	691	164	736
	Avg.	55	150	143	352	150	366

Table 17. (Continued)

Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Dust collector ash	Outlet fly ash
Minor elements (cations)							
Calcium	2	11,200	9,500	24,100	9,200	10,500	7,100
	3	11,300	49,300	35,000	18,700	18,900	17,200
	4	13,500	45,500	49,000	40,900	32,200	34,700
	Avg.	12,000	34,800	36,000	22,900	20,500	19,700
Iron	2	19,500	120,000	190,500	95,500	84,600	84,200
	3	23,600	290,400	258,700	156,600	188,700	131,000
	4	26,600	288,400	313,900	172,600	116,500	124,000
	Avg.	23,200	212,900	254,400	142,600	129,900	113,000
Sulfur	2	26,000	900	4,000		11,000	
	3	38,500	2,200	4,200		3,000	
	4	39,500	1,700	4,800		3,950	
	Avg.	34,700	1,600	4,330		5,980	
Anions							
Chloride	2	396	92	27.5	3,400	62	1,335
	3	43	91	37	808	31	125
	4	18	76.5	88	2,260	12	332
	Avg.	152	87	51	2,160	35	597
Fluoride	2	135	9.0	43.0	796	45.5	830
	3	124	10.6	42.8	564	22.5	559
	4	104	12.3	40.7	512	20.6	624
	Avg.	121	10.5	42.2	624	29.5	671
Nitrate	2		15.5	34.0	178	42.1	103
	3		17.7	28.6	307	27.5	88.8
	4		14.7	18.9	57.6	33.2	64.9
	Avg.		16.0	27.2	181	34.3	85.6

Table 17. (Concluded)

Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Dust collector ash	Outlet fly ash
Sulfate	2		116	7,130	5,570	2,110	3,970
	3		1,090	6,580	7,000	2,520	4,310
	4		818	7,430	8,400	3,510	8,020
	Avg.		675	7,050	6,990	2,710	5,430
Organics[c]							
POM (1)	2	2.5	0.2	ND		0.2	
	3	9.6	ND	ND		0.2	
	4	2.1	ND	ND		0.2	
	Avg.	4.7	< 0.2	ND		0.2	
POM (2)	2	ND	0.2	ND		ND	
	3	ND	ND	ND		ND	
	4	ND	ND	ND		ND	
	Avg.	ND	< 0.2	ND		ND	
POM (3)	2	ND	0.2	ND		ND	
	3	ND	ND	ND		ND	
	4	ND	ND	ND		ND	
	Avg.	ND	< 0.2	ND		ND	
PCB's (all)	2	ND	0.04	0.08		0.16	
	3	ND	ND	0.06		0.04	
	4	ND	0.02	0.12		0.02	
	Avg.	ND	0.02	0.09		0.07	

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a/ Parts per million by weight.

b/ No sample left.

c/ POM compounds:
(1) 7,12-Dimethylbenz[a]anthracene
(2) 3,4-Benzopyrene
(3) 3-Methylcholanthrene

Note: ND = None detected.

Another check of the validity of the measured concentrations can be made by comparing the values found in this study with those found by Oak Ridge National Laboratory (ORNL) in a similar study.[30/] ORNL data are the most comparable that we could find based on the source of coal used in both programs and metals analyzed. ORNL performed all of their analyses by neutron activation, an analysis procedure totally independent from the atomic absorption procedures used in this study.

Table 18 gives a comparison of MRI average values with ORNL values for coal, bottom ash, and inlet and outlet fly ash. Because ORNL tested a cyclone-fed boiler with an electrostatic precipitator, systematic differences may be expected when the ORNL values for outlet fly ash and bottom ash are compared to those reported by MRI. For example, because the control device at Widows Creek was relatively inefficient, metal concentrations in the inlet and outlet fly ash are similar; on the other hand, the more efficient precipitator used in the ORNL study resulted in higher concentrations in the outlet fly ash which was composed of finer particles that were more enriched in trace metals.

The results of the proximate analyses of the coal and ash samples, which were performed by the Industrial Testing Laboratory of Kansas City, are reported in Table 19. One blind duplicate sample of each sample type (i.e., Run 3 coal, Run 3 bottom ash, Run 2 superheater ash, and Run 4 dust collector ash) was submitted for analysis as a precision check. The results obtained for the check samples agreed closely with the duplicates except for the heat of combustion of dust collector ash samples from Run 4. Bottom ash analysis gave negative results for fixed carbon, which is determined by differences; the high iron content caused these samples to gain weight during ignition due to the formation of iron oxides.

Flue Gas Samples

Mass-Rate Sampling Train - The quantities of total particulates and hazardous pollutants which were found in the flue gas sampling trains operated at the inlet and outlet of the dust collector are given in Tables 20 through 26. Some of the results from hazardous pollutants are suspect because of problems encountered in operating the sampling trains as discussed below.

Table 18. COMPARISON OF RESULTS WITH ORNL[30] DATA

		Pollutant concentrations (ppm)			
Trace metal		Coal	Bottom ash	Inlet fly ash	Outlet fly ash
Antimony	MRI	< 1.1	1.3	< 0.95	1.5
	ORNL	0.5	0.04	12	440
Arsenic	MRI	14.3	5.8	8.4	8.9
	ORNL	14	10	120	440
Barium	MRI	< 168	731	881	1,074
	ORNL	59	440	450	750
Beryllium	MRI	1.5	7.3	8.0	9.3
	ORNL	[a]	[a]	[a]	[a]
Cadmium	MRI	0.99	1.08	6.44	8.09
	ORNL	0.46	1.1	8.0	51
Chromium	MRI	24	124	206	220
	ORNL	20	150	310	900
Cobalt	MRI	1.45	3.63	5.98	3.69
	ORNL	[a]	[a]	[a]	[a]
Copper	MRI	10	48	68	74
	ORNL	[a]	[a]	[a]	[a]
Lead	MRI	3.7	8.1	32.0	36.6
	ORNL	[a]	[a]	[a]	[a]
Manganese	MRI	35	229	249	201
	ORNL	34	300	290	430
Mercury	MRI	1.91	< 0.51	20	17
	ORNL	[a]	[a]	[a]	[a]
Nickel	MRI	15	62	134	126
	ORNL	[a]	[a]	[a]	[a]
Selenium	MRI	< 6.1	< 5.6	26.5	< 16.7
	ORNL	[a]	[a]	[a]	[a]

Table 18. (Concluded)

Trace Metal		Pollutant concentrations (ppm)			
		Coal	Bottom ash	Inlet fly ash	Outlet fly ash
Tellurium	MRI	< 30	43	< 30	< 33
	ORNL	a/	a/	a/	a/
Tin	MRI	1.69	2.03	2.81	1.92
	ORNL	a/	a/	a/	a/
Titanium	MRI	895	6,147	6,448	6,887
	ORNL	510	4,100	6,080	10,000
Vanadium	MRI	62	353	341	415
	ORNL	28	260	440	1,180
Zinc	MRI	55	150	352	366
	ORNL	46	100	740	5,900

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a/ Not determined.

Table 19. COAL AND ASH PROPERTIES

Stream	Run	Percent by weight, as received: Moisture	Ash	Volatile matter	Fixed carbon	Sulfur	Heat of combustion (Btu/lb)
Coal	2	1.25	14.95	32.38	51.42	2.60	12,508
	3	1.59	14.72	36.12	47.57	3.84	11,926
		1.65	14.71	36.07	47.57	3.87	12,041
	4	1.38	17.87	34.35	46.40	3.95	11,541
	Avg.	1.42	15.84	34.28	48.46	3.47	12,011
Bottom ash	2	0.09	a/	1.01	a/	0.09	137
	3	0.01	a/	1.37	a/	0.23	134
		0.13		2.28		0.21	130
	4	0.08	93.79	1.52	4.61	0.17	172
	Avg.	0.08	-	1.45	-	0.16	147
Superheater Ash	2	0.13	94.41	2.82	2.64	0.42	657
		0.14	94.36	2.47	3.03	0.37	614
	3	0.19	95.51	3.40	0.90	0.42	484
	4	0.29	87.76	4.76	7.19	0.48	660
	Avg.	0.21	92.55	3.60	3.64	0.43	593
Dust Collector Ash	2	0.11	90.29	2.15	6.45	1.10	659
	3	0.07	93.21	2.52	4.20	0.30	852
	4	0.10	89.05	3.08	7.77	0.43	1,528
		0.03	91.76	3.31	5.90	0.36	105
	Avg.	0.08	91.30	2.62	5.83	0.60	776

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a/ Ash gained weight due to high iron content.

Table 20. PARTICULATE MASS (GRAMS) COLLECTED IN FLUE GAS SAMPLING TRAIN

	Net weight (g)					
	Run 2		Run 3		Run 4	
Sample	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Probe	18.7677	5.8747	13.[illegible]549	3.3076	19.7028	4.5901
Heated quartz filter	12.3005	8.3259	12.0023	9.0423	13.1129	11.7779
Water impingers	0.1787	0.0816	0.4112	0.0624	0.2279	0.1011
	0.0018	0.0003	0.0037	0.0008	0.0022	0.0015
Impinger rinse	0.0360	0.0314	0.0297	0.0175	0.0595	0.0296
Total	31.2847	14.3139	25.7018	12.4306	33.1053	16.5002

Table 21. POLLUTANT MASS (MICROGRAMS) COLLECTED IN FLUE GAS SAMPLING TRAIN
(Run 2, Dust Collector Inlet)

Pollutant	Probe and cyclone	Filter	Water impingers	Water impinger rinse	Back-up filter	Tenax plug	First acid impinger[b/]	Second acid impinger[b/]	H_2O_2 rinse[b/]
Trace elements (cations)									
Antimony	7.13	9.84					0.78	0.13	0.44
Arsenic	128	128					2.4	2.0	47.4
Barium	19,820	12,920							
Beryllium	143	112							
Cadmium	73.6	63.8							
Chromium	7,390	1,810							
Cobalt	133								
Copper	1,480	861							
Lead	541	138							
Manganese	3,230	1,510							
Mercury	178	341					2.18	1.22	0.96
Nickel	4,620	910							
Selenium	505	363					< 0.50	0.93	1.1
Tellurium	582	381							
Tin	35.1	59.5							
Titanium	118,000	81,400							
Vanadium	5,780	3,780							
Zinc	3,700	1,353							
Minor elements (cations)									
Calcium	191,430	93,480							
Iron	1,850,500	1,115,700							
Anions									
Chloride	100,800	4,690							
Fluoride	16,900	7,850							
Nitrate	4,570	947							
Sulfate	114,900	58,020							
Organics[a/]									
POM (1)	ND	20	ND	ND	ND	ND			
POM (2)	ND	20	ND	ND	ND	ND			
POM (3)	186	39	ND	ND	ND	ND			
PCB's (all)	ND	ND	ND	6.2	ND	5,700			

Note: ND = None Detected

[a/] POM compounds:
(1) 7,12-Dimethylbenz[a]anthracene
(2) 3,4-Benzopyrene
(3) 3-Methylcholanthrene

[b/] Vaporous elements

Table 22. POLLUTANT MASS (MICROGRAMS) COLLECTED IN FLUE GAS SAMPLING TRAIN
(Run 2, Dust Collector Outlet)

Pollutant	Probe and cyclone	Filter	Water impingers	Water impinger rinse	Back-up filter	Tenax plug	First acid impinger[b]	Second acid impinger[b]	H_2O_2 rinse[b]
Trace elements (cations)									
Antimony	5.35	16.6							
Arsenic	31.7	73.3					0.20	0.16	0.42
Barium	5,980	8,630					2.2	1.5	3.3
Beryllium	52.3	89.9							
Cadmium	7.81	81.6							
Chromium	3,125	1,370							
Cobalt	21.4	29.9							
Copper	517	641							
Lead	28.8	236							
Manganese	1,350	982							
Mercury	327	< 4.7							
Nickel	2,340	591					1.08	0.62	0.57
Selenium	36.4	232							
Tellurium	247	< 241					1.7	0.89	1.1
Tin	10.1	14.0							
Titanium	40,450	56,840							
Vanadium	1,770	3,330							
Zinc	1,840	1,170							
Minor elements (cations)									
Calcium	51,100	49,960							
Iron	511,000	686,000							
Anions									
Chloride	17,920	1,082							
Fluoride	5,440	6,360							
Nitrate	792	674							
Sulfate	28,560	27,970							
Organics[a]									
POM (1)	ND	12	ND	ND	ND	ND			
POM (2)	ND	12	ND	ND	ND	ND			
POM (3)	ND	12	ND	1	ND	ND			
PCB's (all)	ND	ND	0.1	ND	0.2	13.2			

Note: ND = None Detected

[a] POM compounds:
(1) 7,12-Dimethylbenz[a]anthracene
(2) 3,4-Benzopyrene
(3) 3-Methylcholanthrene

[b] Vaporous elements

Table 23. POLLUTANT MASS (MICROGRAMS) COLLECTED IN FLUE GAS SAMPLING TRAIN
(Run 3, Dust Collector Inlet)

Pollutant	Probe and cyclone	Filter	Water impingers	Water impinger rinse	Back-up filter	Tenax plug	First acid impinger[b]	Second acid impinger[b]	H_2O_2 rinse[b]
Trace elements (cations)									
Antimony	< 13.3	8.88					0.38	0.36	0.70
Arsenic	96.8	107					68.5	3.6	9.6
Barium	7,300	7,960							
Beryllium	92.8	101							
Cadmium	54.3	51.2							
Chromium	2,480	1,760							
Cobalt	101	62.8							
Copper	862	780							
Lead	350	310							
Manganese	3,300	2,300							
Mercury	297	304					3.4	1.43	0.75
Nickel	2,150	1,090							
Selenium	425	182					1.6	1.5	2.6
Tellurium	411	< 336							
Tin	35.4	48.5							
Titanium	92,400	84,200							
Vanadium	3,300	2,710							
Zinc	2,640	2,450							
Minor elements (cations)									
Calcium	267,700	204,000							
Iron	2,244,000	1,712,000							
Anions									
Chloride	20,100	216							
Fluoride	10,700	3,490							
Nitrate	6,170	1,560							
Sulfate	124,700	52,000							
Organics[a]									
POM (1)	ND	ND	ND	ND	ND	ND			
POM (2)	ND	ND	ND	ND	ND	11.4			
POM (3)	105	23	ND	ND	ND	ND			
PCB's (all)	ND	ND	ND	8.5	0.4	12			

Note: ND = None Detected

a/ POM compounds:
(1) 7,12-Dimethylbenz[a]anthracene
(2) 3,4-Benzopyrene
(3) 3-Methylcholanthrene

b/ Vaporous elements

Table 24. POLLUTANT MASS (MICROGRAMS) COLLECTED IN FLUE GAS SAMPLING TRAIN
(Run 3, Dust Collector Outlet)

Pollutant	Probe and cyclone	Filter	Water impingers	Water impinger rinse	Back-up filter	Tenax plug	First acid impinger[b/]	Second acid impinger[b/]	H_2O_2 rinse[b/]
Trace elements (cations)									
Antimony	4.63	12.1					0.13	0.27	0.67
Arsenic	23.8	44.3					2.9	3.3	3.7
Barium	3,840	11,750							
Beryllium	27.1	77.8							
Cadmium	18.0	29.9							
Chromium	774	1,320							
Cobalt	9.20								
Copper	265	606							
Lead	123	246							
Manganese	691	1,211							
Mercury	21.5	< 5.3					0.41	0.99	0.26
Nickel	409	660							
Selenium	< 20.8	141					1.3	0.87	2.0
Tellurium	162	271							
Tin	5.82	2,360							
Titanium	24,390	67,180							
Vanadium	814	2,430							
Zinc	853	994							
Minor elements (cations)									
Calcium	54,600	158,240							
Iron	447,000	1,167,000							
Anions									
Chloride	456	1,085							
Fluoride	2,600	4,300							
Nitrate	400	697							
Sulfate	21,940	31,240							
Organics[a/]									
POM (1)	ND	15	ND	ND	ND	ND			
POM (2)	ND	30	ND	ND	ND	ND			
POM (3)	ND	45	ND	ND	ND	ND			
PCB's (all)	ND	ND	0.1	7.0	0.2	0.5			

Note: ND = None Detected

a/ POM compounds:
(1) 7,12-Dimethylbenz[a]anthracene
(2) 3,4-Benzopyrene
(3) 3-Methylcholanthrene

b/ Vaporous elements

Table 25. POLLUTANT MASS (MICROGRAMS) COLLECTED IN FLUE GAS SAMPLING TRAIN
(Run 4, Dust Collector Inlet)

Pollutant	Probe and cyclone	Filter	Water impingers	Water impinger rinse	Back-up filter	Tenax plug	First acid impinger[b/]	Second acid impinger[b/]	H_2O_2 rinse[b/]
Trace elements (cations)									
Antimony	< 25.6	15.7					0.09	0.02	0.27
Arsenic	174	138					< 2.96	5.1	6.0
Barium	19,200	13,200							
Beryllium	146	123							
Cadmium	142	210							
Chromium	3,170	1,850							
Cobalt	96.7	46.4							
Copper	1,140	970							
Lead	786	797							
Manganese	7,090	5,075							
Mercury	593	< 7.34					1.42	1.40	0.72
Nickel	1,950	1,230							
Selenium	439	463					0.90	< 1.03	2.7
Tellurium	611	< 380							
Tin	34.9	32.9							
Titanium	114,800	79,900							
Vanadium	8,310	7,380							
Zinc	11,000	11,700							
Minor elements (cations)									
Calcium	782,200	559,900							
Iron	3,420,000	1,718,000							
Anions									
Chloride	55,400	18,750							
Fluoride	11,800	4,980							
Nitrate	1,340	548							
Sulfate	186,300	89,300							
Organics[a/]									
POM (1)	39	ND	ND	ND	ND	ND			
POM (2)	79	ND	ND	ND	ND	ND			
POM (3)	39	18	ND	16	ND	ND			
PCB's (all)	ND	ND	ND	7.9	0.3	ND			

Note: ND = None Detected

[a/] POM compounds:
(1) 7,12-Dimethylbenz[a]anthracene
(2) 3,4-Benzopyrene
(3) 3-Methylcholanthrene

[b/] Vaporous elements

Table 26. POLLUTANT MASS (MICROGRAMS) COLLECTED IN FLUE GAS SAMPLING TRAIN
(Run 4, Dust Collector Outlet)

Pollutant	Probe and cyclone	Filter	Water impingers	Water impinger rinse	Back-up filter	Tenax plug	First acid impinger[b/]	Second acid impinger[b/]	H_2O_2 rinse[b/]
Trace elements (cations)									
Antimony	6.89	c/					0.23	0.28	0.06
Arsenic	33.0	163					1.5	0.9	3.0
Barium	3,140	12,080							
Beryllium	41.3	114							
Cadmium	56.2	174							
Chromium	1,060	1,790							
Cobalt	10.5	66.2							
Copper	349	824							
Lead	288	714							
Manganese	1,500	3,160							
Mercury	10.7	405					0.45	0.43	0.79
Nickel	555	860							
Selenium	83.5	c/					1.5	< 0.51	< 0.51
Tellurium	c/	342							
Tin	7.94	19.7							
Titanium	30,570	74,220							
Vanadium	2,220	7,970							
Zinc	3,390	8,660							
Minor elements (cations)									
Calcium	149,200	418,100							
Iron	633,900	1,401,600							
Anions									
Chloride	464	4,970							
Fluoride	3,270	6,950							
Nitrate	425	638							
Sulfate	30,830	100,500							
Organics[a/]									
POM (1)	45	33	ND	ND	ND	ND			
POM (2)	ND	66	ND	ND	ND	ND			
POM (3)	28	ND	ND	ND	ND	ND			
PCB's (all)	ND	ND	0.1	ND	0.3	ND			

Note: ND = None Detected

a/ POM compounds:
(1) 7,12-Dimethylbenz[a]anthracene
(2) 3,4-Benzopyrene
(3) 3-Methylcholanthrene

b/ Vaporous elements

c/ No sample left.

The water impingers, containing 100 ml of water, could not be maintained at a temperature below 20°C. Recent studies by MRI[31] have shown that these conditions are not satisfactory for efficient condensation of POM and PCB. However, it should be noted from this work that the bulk of the POM is found on the ash collected in the probe and heated filter. The association of POM primarily with ash has been observed in subsequent source testing as reported for Winnetka Organic Test 2.[31]

The results from additional source testing[31] using a Tenax-GC® plug indicate that it is an efficient trap for PCB vapor and the data from Widows Creek should be reliable even though most of the PCB was not condensed in the water impingers.

The acid permanganate impingers did not hold oxidizing strength through any of the three runs on the inlet and outlet, indicating elemental vapor penetration through these impingers. Only four metals (arsenic, antimony, selenium, and mercury) were analyzed in the acid permanganate impingers. In subsequent source tests,[31] we have found that acid permanganate will not trap mercury efficiently at isokinetic sampling rates even if maximum oxidizing strength is maintained. We have also found in tests following the Widows Creek sampling that selenium and antimony are trapped in sodium carbonate solution (not analyzed in this study).

Size Train - The Brink particle size train samples were analyzed for metals from the composite inlet and the composite outlet samples. Because of the low quantities of particulate collected (Table 27) only 15 of the 21 metals were analyzed, i.e., only those elements that can be analyzed by the carbon rod technique. Elemental concentrations on each collection stage are given in Tables 28 and 29. (Brink outlet Stage 2 was contaminated during preparation for hydrofluoric acid digestion.)

The results for the filter are subject to large errors due to high filter to ash weight ratios. Three combined filter-ash samples were digested together because of the difficulty in accurately transferring submilligram quantities of ash from Tissuquartz filters. Therefore, relatively high background values had to be subtracted from elements detected.

Table 27. PARTICULATE MASS (GRAMS) COLLECTED IN THE PARTICLE SIZE TRAIN

	Inlet weights (g)				Weight (%)	
Stage	Run 2	Run 3	Run 4	Total	All stages	Plates only
Cyclone	0.09010	0.08628	0.09790	0.27428	77.55	
1	0.01200	0.01394	0.01821	0.04415	12.48	58.47
2	0.01187	0.00561	0.00766	0.02514	7.11	33.29
3	0.00134	0.00110	0.00224	0.00468	1.32	6.20
4	0.00023	0.00034	0.00059	0.00116	0.33	1.54
5	0.00013	0.00009	0.00016	0.00038	0.11	0.50
Back-up filter	0.00150	0.00100	0.00140	0.00390	1.10	
Total				0.35369		
	Outlet weights (g)					
Cyclone	0.05620	0.05296	0.04302	0.15218	79.67	
1	0.00971	0.00748	0.00643	0.02362	12.37	66.26
2	0.00253	0.00194	0.00401	0.00848	4.44	23.79
3	0.00064	0.00044	0.00086	0.00194	1.02	5.44
4	0.00052	0.00013	0.00052	0.00117	0.61	3.29
5	0.00027	0.00012	0.00004	0.00043	0.22	1.21
Back-up filter	0.00120	0.00160	0.00040	0.00320	1.67	
Total				0.19102		

Table 28. POLLUTANT CONCENTRATION (ppm)[a] VERSUS PARTICLE SIZE COMPOSITE OF DUST COLLECTOR INLET SAMPLES

Pollutant	Cyclone	Stage 1 (> 3.96 µm)	Stage 2 (2.35 to 3.96 µm)	Stage 3 (1.61 to 2.35 µm)	Stage 4 (0.87 to 1.61 µm)	Stage 5 (0.56 to 0.87 µm)	Back-up filter
Trace elements (cations)							
Beryllium	6.6	5.2	8.7	4.7	5.4	36.1	97
Cadmium	58	46	164	92	135	447	571
Chromium	381	251	458	1,080	3,080	4,510	1,740
Cobalt	29	26	30	28	58	75	66
Copper	75	147	261	152	564	2,660	3,380
Lead	13.4	14.5	15.5	29.5	12.1	18.4	10.2
Manganese	178	149	274	189	569	654	692
Nickel	450	460	840	690	2,460	689	1,380
Tellurium	3.5	2.3	2.3	3.1	6.6	17.4	41
Thallium	1.2	1.2	1.4	2.1	4.7	28	55
Tin	4.0	9.3	7.6	4.3	10.3	52	32.8
Vanadium	422	475	818	592	741	1,550	1,970
Zinc	426	791	1,110	781	2,670	4,620	4,100
Minor elements (cations)							
Calcium	23,000	20,000	35,000	20,000	80,000	81,000	133,000
Iron	134,000	145,000	155,000	295,000	121,000	184,000	102,000

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[a] Parts per million by weight.

Table 29. POLLUTANT CONCENTRATION (ppm)[a] VERSUS PARTICLE SIZE COMPOSITE OF DUST COLLECTOR OUTLET SAMPLES

Pollutant	Cyclone	Stage 1 (> 2.87 µm)	Stage 2[b] (1.69 to 2.87 µm)	Stage 3 (1.16 to 1.69 µm)	Stage 4 (0.61 to 1.16 µm)	Stage 5 (0.39 to 0.61 µm)	Back-up filter
Trace elements (cations)							
Beryllium	8.5	12.6		8.3	3.5	86	88
Cadmium	36	80		165	435	429	312
Chromium	284	347		577	709	1,790	2,030
Cobalt	46	55		48	67	218	65
Copper	183	177		212	264	4,500	4,120
Lead	12.6	10.5		9.3	6.8	18.5	6.2
Manganese	154	199		288	376	1,560	656
Nickel	401	414		319	478	512	437
Tellurium	1.8	2.5		6.7	11.2	22.1	22.8
Thallium	1.8	1.3		2.9	4.5	9.3	30.9
Tin	3.0	5.1		13.4	14.5	69.7	9.4
Vanadium	278	630		500	680	1,660	1,970
Zinc	876	1,780		2,260	1,880	4,640	3,130
Minor elements (cations)							
Calcium	28,000	35,000		47,000	100,000	169,000	159,000
Iron	126,000	105,000		93,000	68,000	185,000	62,000

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[a] Parts per million by weight.

[b] Sample contaminated during digestion.

Samples from Brink Stages 4 and 5 were less than 2 mg after composite samples were made. The samples had to be digested and brought to known volume before analysis. The smallest volume was 1 ml which resulted in a large dilution factor for these samples. Weighing error, in combination with the high dilution factor, made accurate analysis of these samples impossible.

ANALYTICAL QUALITY ASSURANCE

Table 30 presents the results of the precision, recovery and accuracy determinations made during the analysis of the Widows Creek samples.

Precision

Duplicate analyses were performed on coal, bottom ash, superheater ash, and dust collector ash from each of the three runs. These duplicate samples were taken through the entire digestion and analysis procedures. Precision values are reported as a pooled relative standard deviation (PRSD) for each analysis because of the small number of analyses for any given sample and the relatively large number of duplicate analyses performed for any given element.

The standard deviation for the duplicate samples was calculated by:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{2} (x_i - \bar{x})^2}{0.889}}$$

The pooled relative standard deviation was then calculated by the following equation:

$$\mathrm{PRSD} = \sqrt{\frac{\sum_{i=1}^{N} \mathrm{RSD}_i^{\,2}}{N}}$$

Table 30. QUALITY ASSURANCE DATA

Pollutant	Pooled relative standard deviation of duplicate analyses (%)	Average percent recovery from fortified samples	Percent of NBS certified values: Coal	Percent of NBS certified values: Fly ash
Trace elements (cations)				
Antimony	12.5	82	c/	c/
Arsenic	12.2	a/	d/	d/
Barium	11.9	85	c/	c/
Beryllium	2.0	83	153	108
Cadmium	8.6	94	c/	d/
Chromium	7.8	99	120	90
Cobalt	9.8	a/	c/	c/
Copper	5.8	88	33	94
Lead	11.8	a/	166	111
Manganese	2.8	90	85	59
Mercury	2.9	90	d/	d/
Nickel	5.6	98	106	118
Selenium	15.7	80	d/	d/
Tellurium	12.8	b/	c/	c/
Tin	11.2	b/	100	c/
Titantium	5.2	90	c/	c/
Vanadium	3.3	b/	110	94
Zinc	8.9	93	81	81
Minor elements (cations)				
Calcium	4.6	94	c/	c/
Iron	6.4	115		c/
Anions				
Chloride	6.3		c/	c/
Fluoride	7.1		c/	c/
Nitrate			c/	c/
Sulfate			c/	c/
Organics e/				
POM (1)		70	c/	c/
POM (2)			c/	c/
POM (3)			c/	c/
PCB's (all)		103	c/	c/

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a/ Spike too large

b/ Spike too small.

c/ Not certified by the National Bureau of Standards (NBS).

d/ Nonflame AA method.

e/ POM compounds:
  (1) 7,12-Dimethylbenz[a]anthracene
  (2) 3,4-Benzopyrene
  (3) 3-Methylcholanthrene

where N = 8 (two runs and four sample types, i.e., coal, bottom ash, superheated ash, and dust collector ash), and

$$RSD = \left(\frac{\sigma}{\bar{\bar{x}}}\right)100$$

The factor 0.889 is a statistically more valid number to use than the usual factor n-1 when there are only two numbers used to calculate a σ .

At least two-thirds of the elements determined had PRSD less than 10% (Table 30). The maximum PRSD was 15.7% (for selenium). In terms of conventional relative standard deviations, all elemental analyses were below 7%.

Recovery from Fortified Samples

One sample of each solid type was fortified with all 21 metals of interest before the digestion. The fortification level for each metal was estimated from previous reports for that type of sample. The added metal was in the range of 50 to 100% of that expected in the sample. Calculated values for percent recovery averaged for all types of samples are given in Table 30. In five cases the spike was either too large or small to determine recovery.

The samples that were extracted and analyzed for PCB and POM were spiked with Aroclor-1260 and benzo[a]pyrene before extraction. The results for Aroclor-1260 recovery are quite good. The results for benzo[a]pyrene are low (70%), which indicates a problem with the extraction procedure. It has been found that benzo[a]pyrene is unstable during the Soxhlet extraction procedure. Decomposition during extraction would account for the low recovery.

After completion of the analysis of the Widows Creek samples, National Bureau of Standards (NBS) certified Coal No. 1632 and Fly Ash No. 1633 became available (mid-January 1975). Duplicate samples of each material were digested in a manner described in Section IV. These samples were analyzed by flame atomic absorption for the elements certified by NBS. The analyzed percent of the NBS values are also indicated in Table 30. The NBS certification requires a minimum of 250 mg/sample for the certified values to be valid. We could digest only 100 mg of either of the two materials, thus introducing some error in the comparison of our analyses with the certified values.

It was not possible to check certified values for those elements run by carbon rod atomization technique because the instrument used for Widows Creek samples (Varian AA-5) was modified after completion of the project and before receiving the NBS certified samples. The modification included conversion to a Model AA-6 with different photomultiplier, amplifier, and a background corrector. Any analysis of sample by carbon rod with this instrument configuration would not yield valid numbers when compared to those results obtained with the actual Widows Creek samples. The same problem exists with mercury cold vapor and arsenic, selenium, and antimony hydrides, since the Widows Creek samples were analyzed on the instrument prior to modification.

SECTION VIII

CALCULATED TEST RESULTS

This section of the report presents the results calculated from field sampling data and process monitoring data obtained during the Widows Creek test program and from the analytical results presented in the previous section.

BOILER PERFORMANCE

Table 31 summarizes boiler conditions during the Widows Creek sampling program. The boiler was operating near capacity for each of the three runs. Generator load was recorded periodically from the appropriate meter in the boiler control room. The values for the other quantities shown all fall within the expected ranges.

Table 32 gives the coal feed rate and the mass flow rates of the various ash streams for each of the runs. As indicated, approximately half of the ash produced by coal combustion, i.e., input ash, settled either in the furnace bottom hopper or the superheater ash hopper or was accumulated on boiler tubes the remaining half was mobilized to the flue gas stream. For purpose of this study it was estimated that 60% of the settled ash was bottom ash; this estimate was based on (a) reported fly ash emission facors for utility boilers,32/ (b) reported data on rates of soot buildup10/ and (c) the analytical results presented below.

As indicated in Table 32, the collection efficiency of the mechanical fly ash collector was approximately 45%.

Figures 25, 26, and 27 show the variations in the coal feed rate for each of the three runs. In each case the coal feed rate was constant to within plus or minus 4%. Coal feed rate was determined from periodic scale dump counts.

Table 31. BOILER CONDITIONS

Run	Capacity factor (%)	MW Load	Heat input (10^6 Btu/hr)	Heat rate (Btu/kw-hr)	Flue gas generation (dscfm/Mw)	Excess air (%)
2	96	120	1,330	1.11×10^4	2,070	43[a]
3	99	124	1,290	1.04×10^4	1,920	32[a]
4	98	123	1,330	1.09×10^4	2,100	36
Avg.	98	122	1,320	1.08×10^4	2,030	37

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[a] Approximate value.

Table 32. COAL/ASH MASS FLOW RATES--ALL STREAMS

Run	Coal feed rate (tons/hr)	Coal feed rate (kg/min)	Input ash (kg/min)	Settled ash[a] (kg/min)	Inlet fly ash (kg/min)	Collected fly ash[b] (kg/min)	Outlet fly ash (kg/min)	Collection efficiency (%)
2	53.1	803	120	56.3 (47)[c]	63.7 (53)	28.8 (24)	34.9 (29)	45
3	53.8	813	120	64.2 (53)	55.8 (47)	26.5 (22)	29.3 (25)	47
4	57.6	871	156	83.9 (54)	72.1 (46)	31.9 (20)	40.2 (26)	44
Avg.	54.8	829	132	68.1 (52)	63.9 (48)	29.1 (22)	34.8 (26)	45

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[a] Determined by difference: settled ash = input ash - inlet fly ash.

[b] Determined by difference: collected fly ash = inlet fly ash - outlet fly ash.

[c] Values in parenthesis represent percentage of the coal feed rate.

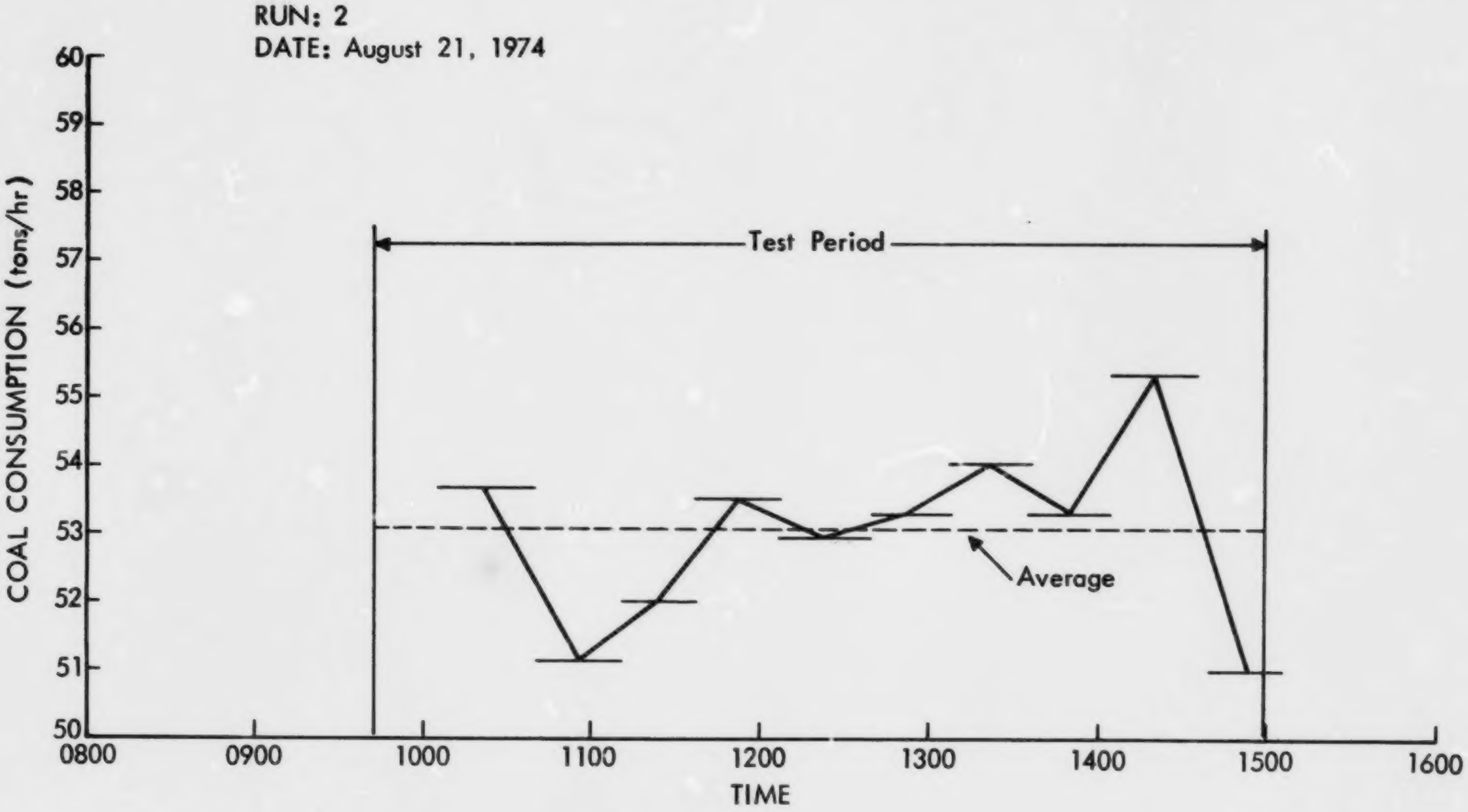

Figure 25. Variations in coal feed rate - Run 2.

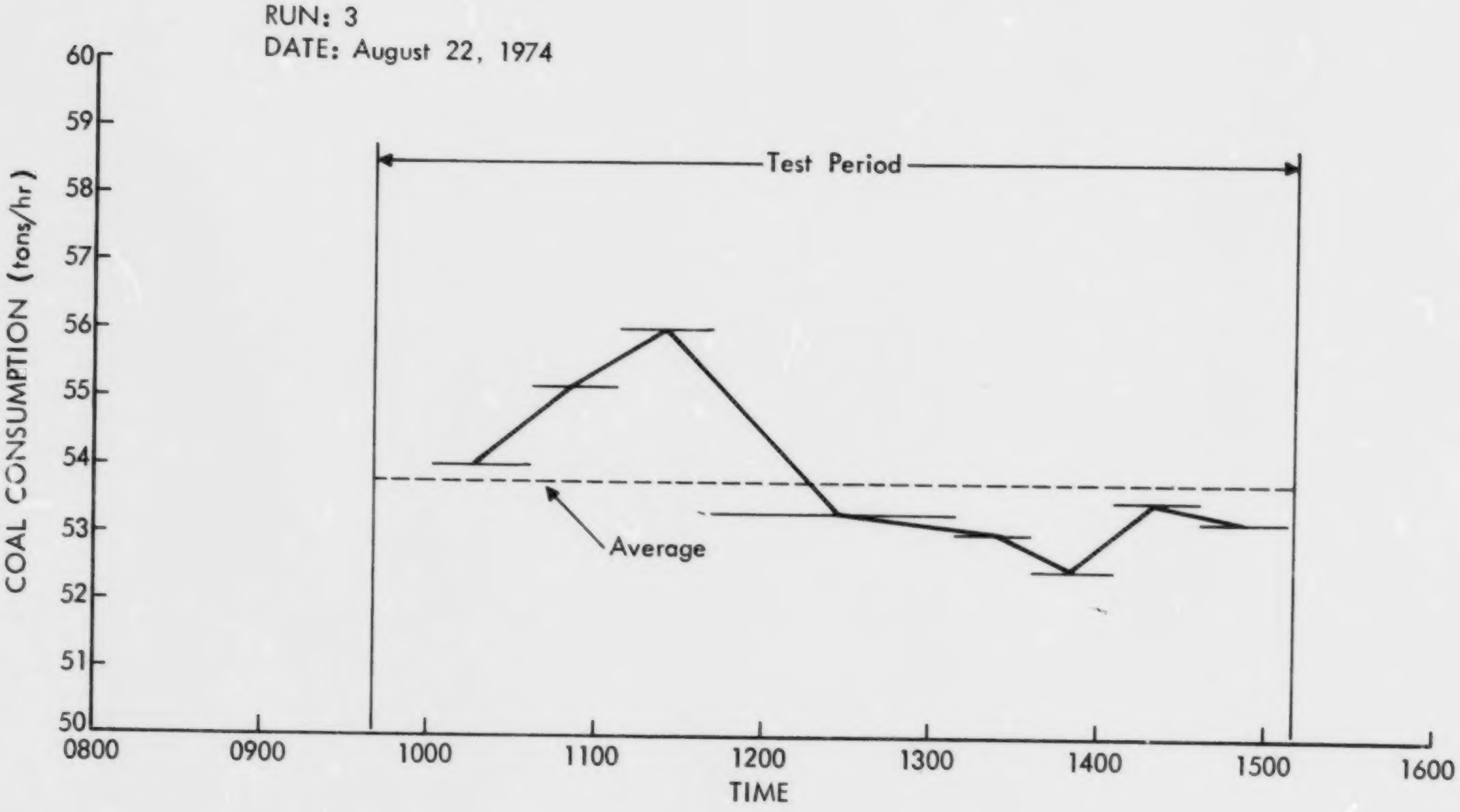

Figure 26. Variations in coal feed rate - Run 3.

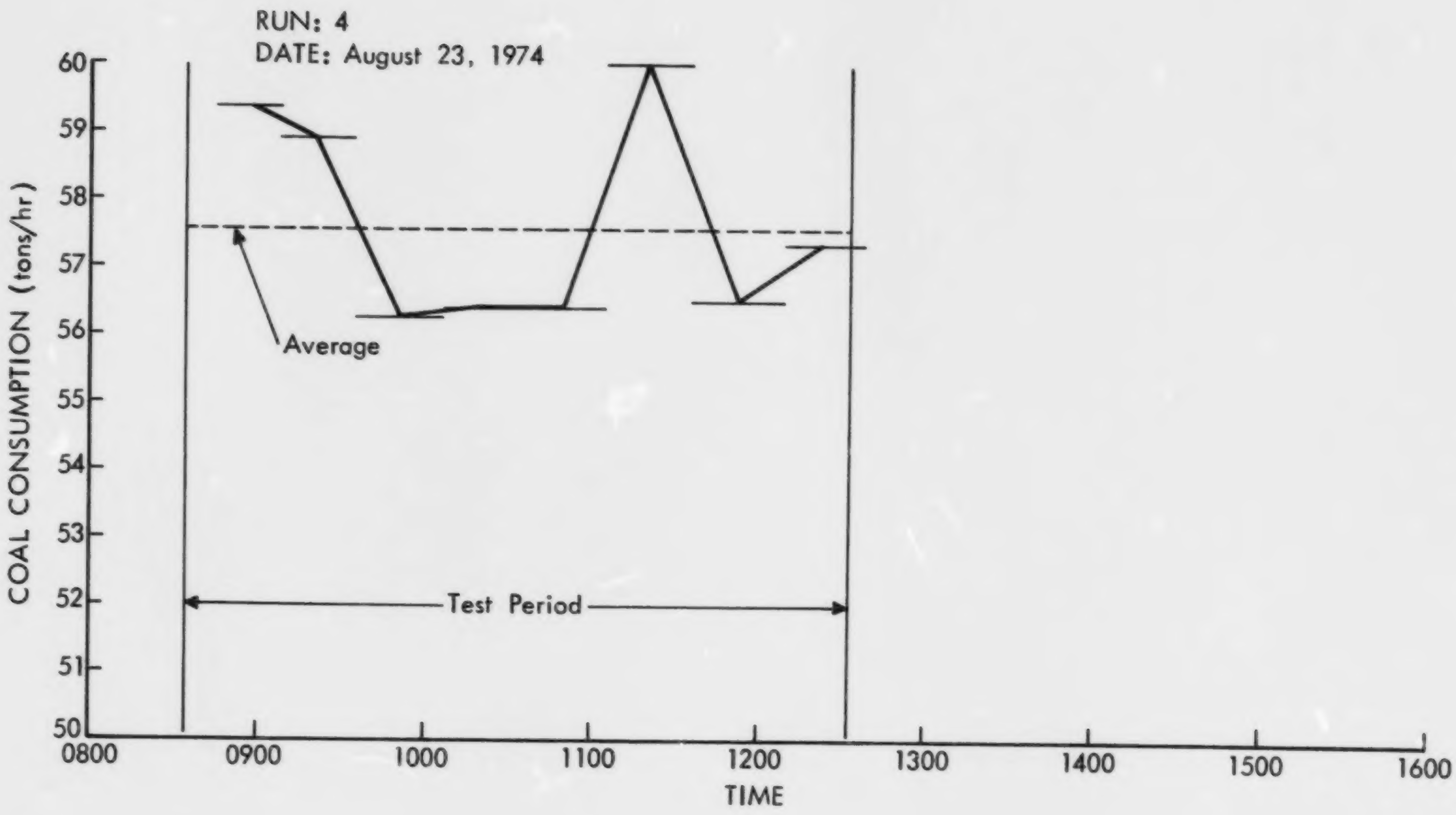

Figure 27. Variations in coal feed rate - Run 4.

Table 33 summarizes the boiler flue gas conditions. As indicated, there was a measured air infiltration (leakage) rate of about 20% between the dust collector inlet sampling locations and the stack. The measurement of excess air obtained upstream of the air heater during Run 4 indicated an additional leakage of about 7% in the air heater.

Boiler steam efficiency was determined for Run 4 using the abbreviated heat loss method specified in ASME Performance Test Code 4.1 (1964). The calculated value of 88.1% is close to the design value for Unit 5. The calculation scheme is presented in detail in Appendix C.

STACK GASES AND INLET AIR

Table 34 gives the breakdown of major components in the stack gases as determined for each run. Also given are the concentrations of sulfur dioxide, nitrogen oxides, and total particulate matter in the stack gases.

Table 35 gives the concentration of total suspended particulates in the air which was drawn into the combustion system. The grain loading in the inlet air was about 0.1% of the grain loading in the stack gases.

PARTICLE SIZE DISTRIBUTION

Table 36 lists the data used for the calculation of particle size distributions. Included are effective cutoff diameters for each stage of the Brink impactor. These values were calculated from particle size sampling parameters and impactor design data for each stage.

The particle size distributions are plotted in Figures 28 and 29.

HAZARDOUS POLLUTANTS

Table 37 gives the calculated flow rates of hazardous pollutants in each of the process flow streams. Also shown is the efficiency of removal of each pollutant from the flue gases by the mechanical dust collector.

Table 33. FLUE GAS CONDITIONS

Run	Location	Flue gas temperature (°F)	Static pressure (in. Hg)	Flow rate (dscfm)	Leakage (dscfm)	Excess air (%)	Particulate loading (gr/acf)
2	Inlet A	376	-0.55	126,000		54	2.05
	Inlet B	387	-0.55	141,000			
	Outlet	367	-0.05	331,000	64,000	92	0.984
3	Inlet A	364	-0.55	114,000		42	1.95
	Inlet B	362	-0.55	141,000			
	Outlet	339	-0.05	306,000	51,000	73	0.916
4	Inlet A	367	-0.55	130,000		52	2.31
	Inlet B	355	-0.55	147,000			
	Outlet	353	-0.05	313,000	36,000	74	1.19

Table 34. STACK GAS COMPOSITION

	Units	Run 2	 3	 4
CO_2	% by volume	8.5	9.2	9.4
O_2	% by volume	9.8	8.5	8.4
CO	% by volume	0.2	0.2	0.1
N_2	% by volume	76.3	75.6	74.9
Moisture	% by volume	5.2	6.5	7.2
SO_2	ppm by volume	1,370	2,350	1,950
NO_x, as NO_2	ppm by volume	303	271	380[a]
Particulate loading	gr/acf	0.984	0.916	1.19

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[a] Estimated value.

Table 35. INLET AIR TSP CONCENTRATIONS

Run	Vol. of air sampled (m^3)	Total particulate collected (mg)	TSP concentration	
			$\mu g/m^3$	gr/acf
2	322	719.7	2,235	9.77×10^{-4}
3	337	617.8	1,831	8.00×10^{-4}
4	245	498.5	2,032	8.88×10^{-4}
Avg.			2,033	8.88×10^{-4}

Table 36. CALCULATED PARTICLE SIZE DISTRIBUTIONS

	Inlet			Outlet		
	ECD	Cumulative weight %		ECD	Cumulative weight %	
Stage	(μm)	All stages	Plates only	(μm)	All stages	Plates only
Cyclone	7.5	77.55		7.5	79.67	
1	3.96	90.03	58.47	2.87	92.04	66.27
2	2.35	97.14	91.76	1.69	96.48	90.06
3	1.61	98.46	97.96	1.16	97.50	95.50
4	0.87	98.79	99.50	0.61	98.11	98.79
5	0.56	98.90	100.00	0.39	98.33	100.00
Filter		100.00			100.00	

Note: ECD = Effective Cutoff Diameter, in microns.

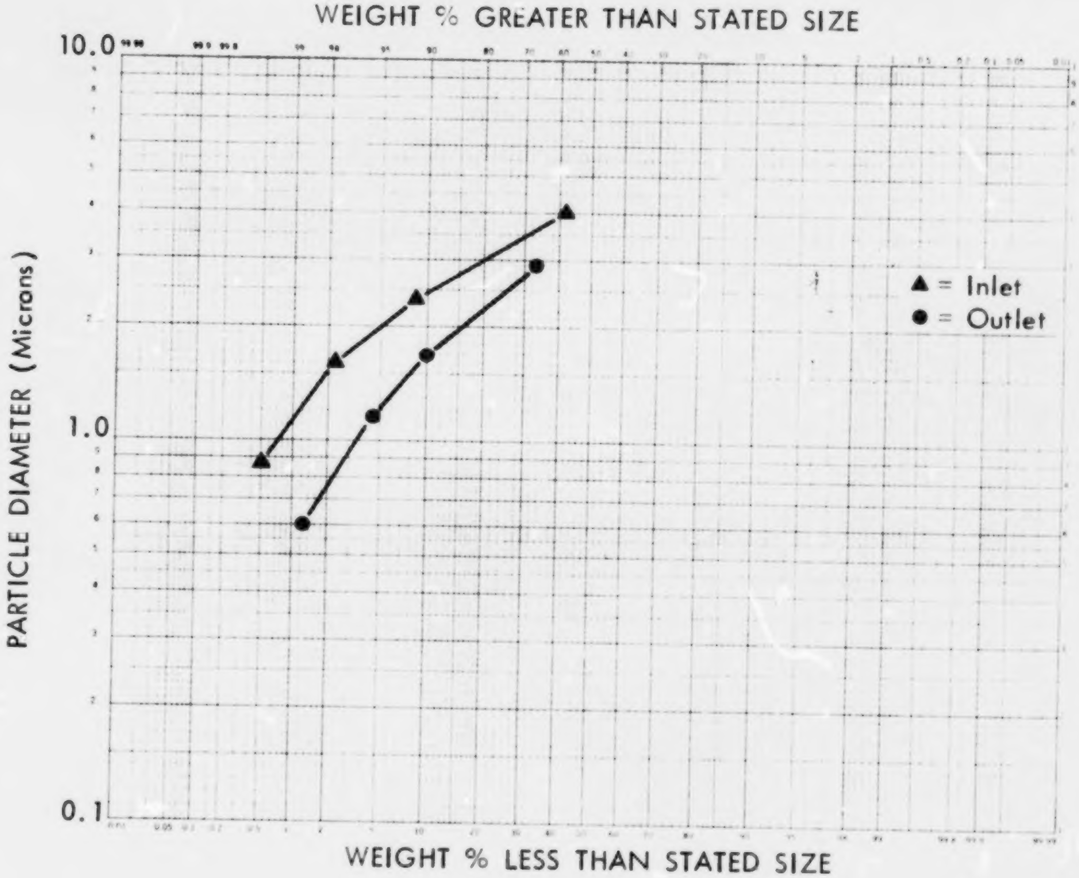

Figure 28. Particle size distribution - plates only.

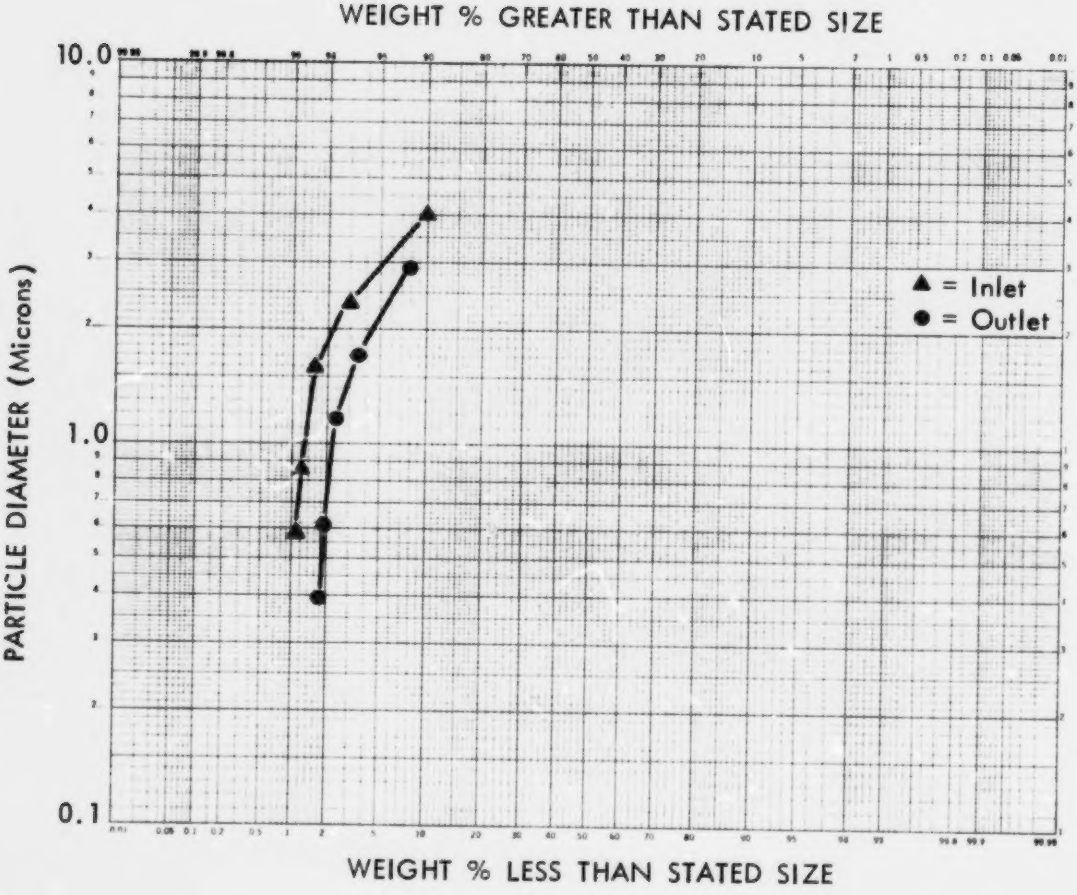

Figure 29. Particle size distribution - all stages.

Table 37. POLLUTANT MASS FLOW RATE (gm/min) IN COAL, ASH, AND FLUE GAS STREAMS

		Pollutant mass flow rate (gm/min)									
Pollutant	Run	Coal	Bottom ash	Superheater ash	Inlet fly ash	Inlet vapor	Dust collector ash[a/]	Outlet fly ash	Outlet vapor	Dust collector efficiency (%)[b/]	Overall mass imbalance (%)
Trace elements (cations)											
Antimony	2	< 1.04	0.044	0.007	0.0350	0.0027	-	0.0537	0.0019	-	-80
	3	0.569	0.054	0.033	< 0.0558	0.0031	0.037	0.0398	0.0025	~ 29	-71
	4	< 1.05	0.065	0.037	< 0.0937	0.0008	0.010	0.0603	0.0014	~ 36	-67
	Avg.	< 0.89	0.054	0.026	< 0.062	0.0022	0.024	0.0513	0.0019	~ 17	-72
Arsenic	2	10.4	0.189	0.272	0.522	0.106	-	0.258	0.0171	51	-93
	3	11.0	0.293	0.082	0.452	0.177	-	0.161	0.0236	64	-95
	4	14.2	0.211	0.191	0.634	< 0.031	-	0.482	0.0132	24	-94
	Avg.	11.9	0.231	0.182	0.536	< 0.105	-	0.300	0.0180	44	-94
Barium	2	< 134	30.6	25.2	66		34.9	36		45	89
	3	< 141	32.5	15.2	34		24.3	37		0	55
	4	< 144	22.4	24.0	71		43.6	37		48	76
	Avg.	< 140	28.5	21.5	57		34.3	37		35	73
Beryllium	2	1.28	0.270	0.144	0.522		0.207	0.349		33	-24
	3	1.22	0.285	0.144	0.430		0.180	0.249		42	-30
	4	1.22	0.327	0.208	0.591		0.309	0.382		35	0
	Avg.	1.24	0.294	0.165	0.514		0.232	0.327		36	-18
Cadmium	2	1.00	0.017	0.033	0.282		0.083	0.219		22	-65
	3	0.252	0.077	0.035	0.233		0.030	0.144		51	2
	4	1.22	0.037	0.066	0.744		0.064	0.566		27	-40
	Avg.	0.824	0.044	0.045	0.420		0.059	0.300		29	-46
Chromium	2	19.3	4.22	2.45	18.9		3.83	11.0		42	11
	3	19.5	5.08	3.03	9.37		5.06	4.98		47	-7
	4	20.0	5.84	4.36	11.0		4.08	6.99		36	6
	Avg.	19.6	5.05	3.28	13.1		4.32	7.66		42	4
Cobalt	2	1.48	0.194	0.132	0.452		0.302	0.126		72	-49
	3	1.23	0.075	0.144	0.362		0.182	0.081		78	-63
	4	0.862	0.161	0.132	0.314		0.204	0.188		40	-21
	Avg.	1.19	0.143	0.126	0.376		0.229	0.132		65	-47

Table 37. (Continued)

Pollutant	Run	Pollutant mass flow rate (gm/min)								Dust collector efficiency (%)[b]	Overall mass imbalance (%)
		Coal	Bottom ash	Superheater ash	Inlet fly ash	Inlet vapor	Dust collector ash[a]	Outlet fly ash	Outlet vapor		
Copper	2	8.03	1.72	1.22	4.78		1.70	2.83		41	-7
	3	9.76	1.85	1.18	3.63		1.96	2.05		44	-28
	4	7.84	2.27	1.51	4.61		1.24	2.89		37	1
	Avg.	8.54	1.95	1.30	4.34		1.63	2.59		40	-12
Lead	2	2.96	0.234	0.268	1.40		0.625	0.653		53	-40
	3	1.84	0.412	0.270	1.46		0.307	0.876		40	1
	4	4.55	0.255	0.316	3.48		0.367	2.46		29	-25
	Avg.	3.12	0.300	0.285	2.11		0.433	1.33		37	-25
Manganese	2	19.3	4.22	4.89	9.75		4.87	5.72		41	2
	3	24.4	14.5	6.81	12.4		7.61	4.51		64	48
	4	44.4	9.26	10.9	26.7		8.55	11.5		57	-9
	Avg.	29.4	9.33	7.53	16.3		7.01	7.24		56	6
Mercury	2	1.51	< 0.018	< 0.013	1.06	0.0089	< 0.035	0.813	0.0055	23	-44
	3	1.55	< 0.019	0.177	1.33	0.0117	< 0.031	0.064	0.0040	95	-83
	4	1.68	< 0.028	1.56	1.32	0.0077	< 0.037	1.02	0.0041	23	56
	Avg.	1.58	< 0.022	< 0.58	1.24	0.0094	< 0.034	0.63	0.0045	49	-63[c]
Nickel	2	14.5	1.52	2.43	11.3		2.53	7.19		36	-6
	3	13.0	3.24	2.41	7.14		2.60	2.52		65	-17
	4	10.5	2.92	3.42	6.99		1.91	3.46		51	12
	Avg.	12.7	2.56	2.75	8.48		2.35	4.39		48	-5
Selenium	2	< 4.90	< 0.186	< 0.140	1.78	< 0.0052	-	0.660	0.0090	> 63	-66
	3	< 4.90	< 0.23	< 0.146	1.34	0.0124	-	< 0.384	0.0099	> 71	-84
	4	5.23	< 0.272	< 0.185	1.98	< 0.0101	< 0.399	0.734	< 0.0062	63	-78
	Avg.	< 5.01	< 0.229	< 0.157	1.70	< 0.0092	< 0.399	< 0.592	< 0.0084	~ 65	-76
Tellurium	2	< 24.1	2.09	0.676	1.97		0.864	< 1.22		38	-65
	3	< 24.4	1.58	< 0.69	< 1.67		0.82	1.03		38	-69
	4	< 26.1	1.31	< 0.906	< 2.16		0.893	1.17		46	-71
	Avg.	< 24.9	1.66	< 0.757	< 1.93		0.859	< 1.14		41	-68

Table 37. (Continued)

Pollutant	Run	Pollutant mass flow rate (mg/min) Coal	Bottom ash	Superheater ash	Inlet fly ash	Inlet vapor	Dust collector ash[a/]	Outlet fly ash	Outlet vapor	Dust collector efficiency (%)[b/]	Overall mass imbalance (%)
Tin	2	1.39	0.096	0.048	0.194		0.050	0.059		70	-82
	3	1.38	0.070	0.041	0.185		0.092	0.070		62	-80
	4	1.44	0.073	0.070	0.149		0.110	0.068		54	-78
	Avg.	1.40	0.080	0.053	0.176		0.084	0.066		62	-80
Titanium	2	878	233	122	409		148	239		42	-15
	3	677	213	141	390		166	217		44	9
	4	660	303	174	428		126	257		40	30
	Avg.	738	250	146	409		147	238		42	6
Vanadium	2	49.0	9.19	5.16	19.6		7.92	12.5		36	-29
	3	49.6	16.1	5.52	13.3		5.04	7.68		42	-31
	4	55.7	18.6	11.5	34.5		7.66	25.0		28	13
	Avg.	51.4	14.6	7.39	22.5		6.87	15.1		33	-14
Zinc	2	28.9	2.29	3.00	10.4		4.44	7.40		29	-41
	3	13.8	10.6	2.82	11.2		3.47	4.39		61	54
	4	96.7	5.39	6.24	49.8		5.23	29.6		70	-52
	Avg.	46.5	6.09	4.02	23.8		4.38	13.8		42	-39
Minor elements (cations)											
Calcium	2	8,990	321	543	586		302	247		58	-84
	3	9,190	1,900	900	1,040		501	504		52	-59
	4	11,800	2,290	1,640	2,280		1,030	1,400		39	-46
	Avg.	9,990	1,500	1,030	1,300		611	717		45	-61
Iron	2	15,700	4,050	4,290	6,080		2,440	2,940		52	-12
	3	19,200	11,200	6,640	8,740		5,000	3,840		56	39
	4	23,200	11,500	10,500	12,400		3,720	4,990		60	33
	Avg.	19,400	8,920	7,140	9,070		3,720	3,920		57	22
Sulfur	2	20,900	50.7	225	-		317		18,000	-	-11
	3	31,300	159	303	-		79.5		29,100	-	-5
	4	34,400	143	403	-		128		24,900	-	-26
	Avg.	28,900	118	310	-		175		24,000	-	-15

Table 37. (Concluded)

Pollutant	Run	Pollutant mass flow rate (gm/min)								Dust collector efficiency (%) [b]	Overall mass imbalance (%)
		Coal	Bottom ash	Superheater ash	Inlet fly ash	Inlet vapor	Dust collector ash[a]	Outlet fly ash	Outlet vapor		
Anions											
Chloride	2	318	3.11	0.619	217		1.79	46.6		79	-84
	3	35.0	3.51	0.95	45.1		0.822	3.66		92	-74
	4	15.7	3.85	2.95	163		0.383	13.3		92	30
	Avg.	123	3.49	1.51	142		0.998	21.2		85	-78
Fluoride	2	108	0.30	0.968	50.7		1.31	29.0		43	-71
	3	101	0.408	1.10	31.5		0.596	16.4		48	-82
	4	90.6	0.619	1.37	28.6		0.657	25.1		12	-69
	Avg.	99.9	0.442	1.15	36.9		0.854	23.5		36	-74

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[a] Superheater ash includes soot build-up.

[b] Average collection efficiency based on average inlet and average outlet values.

[c] Based on two runs only.

Table 38 lists the mass imbalances (averaged for the three runs) for each of the pollutants. Mass imbalance is a measure of the degree to which the output pollutant mass flow rates match the corresponding input values. This may be mathematically expressed as follows:

$$\text{Mass imbalance } (\%) = \frac{\text{output - input}}{\text{input}} \times 100$$

The average mass imbalance for the three runs was calculated based on average inlet and average outlet values; all "less than" (<) values were considered as one-half the value.

As shown in Table 38, nearly all of the mass imbalances values are negative, indicating that there was less mass flow measured in the various output streams than in the input stream. This would be expected, for example, for those trace elements which are highly concentrated in the vaporous state, and inefficiently sampled in the output streams. Values for mass imbalance around the dust collector were consistently smaller in magnitude than corresponding values around the boiler. The overall mass imbalances are heavily weighted by the respective boiler imbalances.

Figures 30, 31, and 32 illustrate the range of mass imbalance values obtained for the three runs. Again the ranges are smallest for mass balance around the dust collector.

Table 39 gives the uncontrolled emissions factors for the elemental pollutants in particulate form. These factors represent the degree to which each element present in coal is converted to fly ash in the flue gas stream. These emission factors do not account for significant amounts of vapors. From another MRI study[33] approximately 90 to 100% of arsenic, mercury, and selenium should exist in the vaporous state.

Table 40 gives the progressive enrichment ratios for each ash stream scaled against the ratio of the hypothetical concentration in coal ash divided by the concentration of the element in coal. The concentration in coal ash is the value that would occur assuming that all of the element were retained in the ash after combustion.

Tables 28 and 29, presented earlier, exhibit a strong tendency for trace metal enrichment with decreasing particle size.

Table 38. AVERAGE MASS IMBALANCES--ALL RUNS

	Mass imbalance (%)		
Pollutant	Boiler	Dust collector	Overall
Trace elements (cations)			
Antimony	-83	78	-72
Arsenic	-90	-50	-94
Barium	53	24	73
Beryllium	-21	9	-18
Cadmium	-38	-15	-46
Chromium	9	-8	4
Cobalt	-46	-4	-47
Copper	-11	-3	-12
Lead	-13	-17	-25
Manganese	13	-12	6
Mercury	-15[a]	-62[a]	-63[a]
Nickel	9	-21	- 5
Selenium	-44	-65	-76
Tellurium	-72	39	-68
Tin	-78	-15	-80
Titanium	9	-6	6
Vanadium	-13	-3	-14
Zinc	-27	-24	-39
Minor elements (cations)			
Calcium	-62	2	-61
Iron	29	-16	22
Sulfur	-	-	-15
Anions			
Chloride	20	-84	-78
Fluoride	-61	-34	-74

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[a] Based on Runs 2 and 3 only.

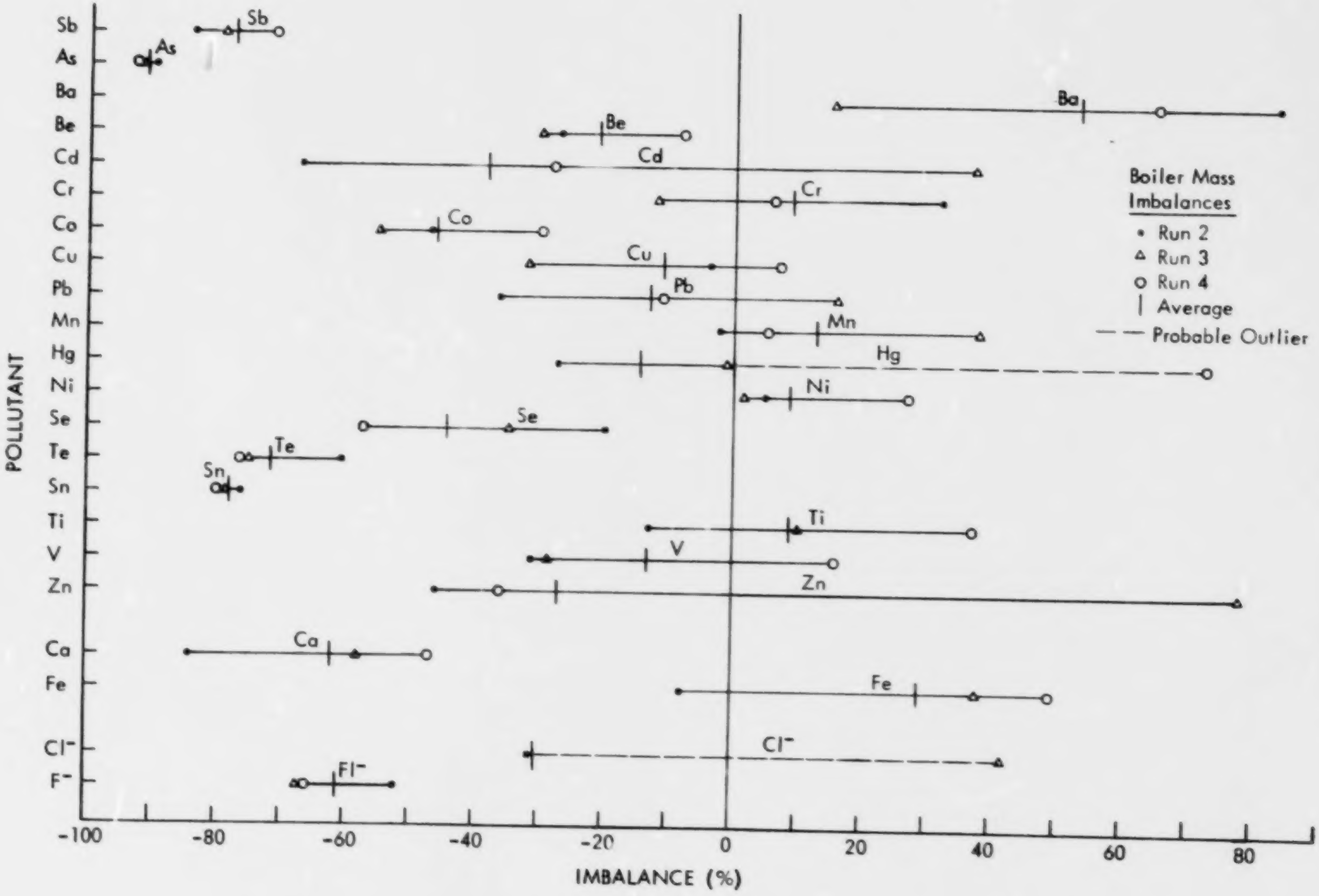

Figure 30. Boiler mass imbalances.

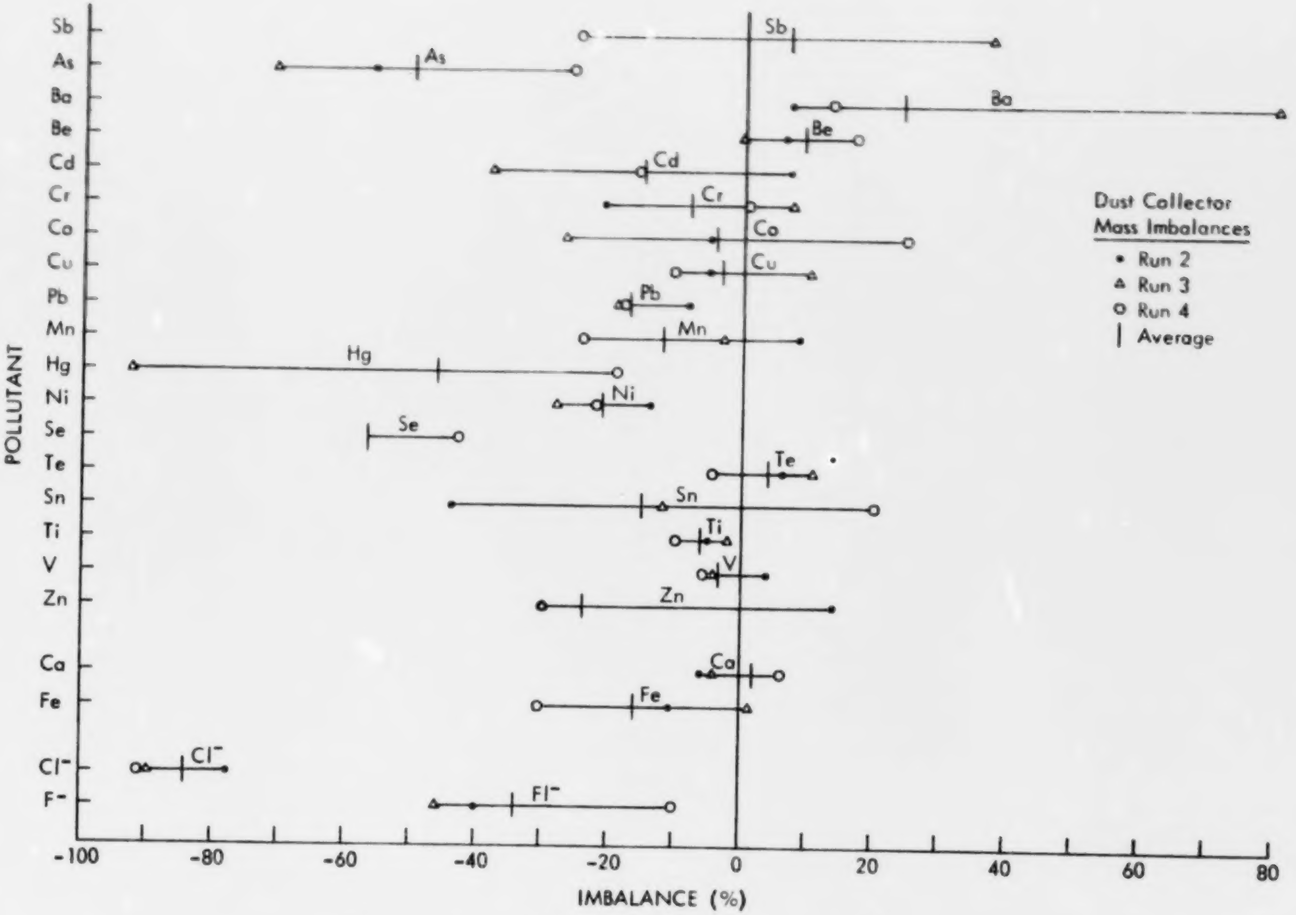

Figure 31. Dust collector mass imbalances.

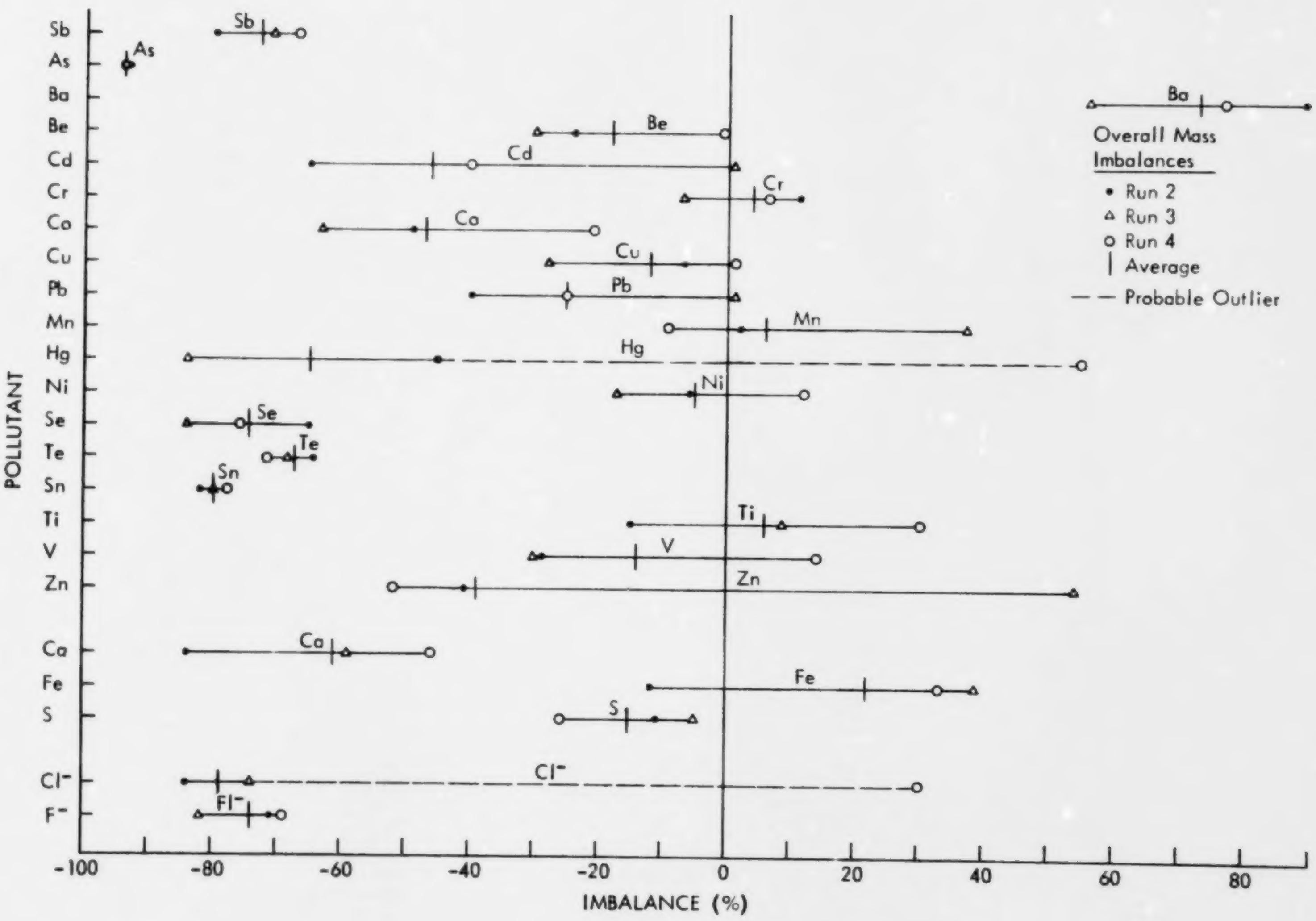

Figure 32. Overall mass imbalances.

Table 39. UNCONTROLLED PARTICULATE EMISSION FACTORS

Pollutant	Particulate emission factor (%)			
	Run 2	Run 3	Run 4	Average[a]
Trace elements (cations)				
Antimony	> 3.37	< 0.81	< 8.92	~ 7.0
Arsenic	5.02	4.11	4.46	4.5
Barium	> 49.3	> 24.1	> 49.3	> 40.7
Beryllium	40.8	35.2	48.4	41.5
Cadmium	28.2	92.5	61.0	51.0
Chromium	97.9	48.1	55.0	66.8
Cobalt	30.5	29.4	36.4	31.6
Copper	59.5	37.2	58.8	50.8
Lead	47.3	79.3	76.5	67.6
Manganese	50.5	50.8	60.1	55.4
Mercury	70.2	85.8	78.6	78.5
Nickel	77.9	54.9	66.6	66.8
Selenium	> 36	> 27	37.9	> 34
Tellurium	> 8.2	~ 6.8	~ 8.3	~ 7.8
Tin	14.0	13.4	10.3	12.6
Titanium	46.6	57.6	64.8	55.4
Vanadium	40.0	26.8	61.9	43.8
Zinc	36.0	81.1	51.5	51.2
Minor elements (cations)				
Calcium	6.52	11.3	19.3	13.0
Iron	38.7	45.5	53.4	46.8
Anions				
Chloride	68.2	129	1,040	115
Fluoride	46.9	31.2	31.6	36.9

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[a] Based on $\frac{\text{average inlet fly ash}}{\text{average coal}}$

Note: Emission factor = $\frac{\text{inlet fly ash}}{\text{coal}} \times 100$

Table 40. POLLUTANT ENRICHMENT RATIOS--AVERAGE, ALL RUNS

Pollutant	Coal ash[a]	Bottom ash / coal ash	Superheater ash / coal ash	Inlet fly ash / coal ash	Dust collector ash / coal ash	Outlet fly ash / coal ash
Trace elements (cations)						
Antimony	< 6.7	0.21	0.14	< 0.15	< 0.143	0.24
Arsenic	90	0.064	0.078	0.093	-	0.092
Barium	< 1,072	> 0.68	> 0.75	> 0.82	> 1.1	> 1.0
Beryllium	9.58	0.76	0.64	0.83	0.82	0.97
Cadmium	6.1	0.18	0.26	1.1	0.33	1.3
Chromium	151	0.82	0.76	1.4	1.0	1.5
Cobalt	9.38	0.39	0.51	0.64	0.85	0.39
Copper	66.3	0.72	0.72	1.0	0.86	1.1
Lead	23.1	0.35	0.46	1.4	0.65	1.6
Manganese	217	1.1	1.2	1.1	1.1	0.93
Mercury	12.1	0.04	1.5	1.7	< 0.10	1.4
Nickel	98.7	0.63	1.0	1.4	0.83	1.3
Selenium	< 38.6	0.15	0.15	> 0.69	0.32	0.43
Tellurium	191	> 0.23	0.15	0.16	> 0.16	0.17
Tin	10.8	0.19	0.18	0.26	0.27	0.18
Titanium	5,740	1.1	0.93	1.1	0.89	1.2
Vanadium	394	0.90	0.66	0.87	0.60	1.1
Zinc	326	0.46	0.44	1.1	0.46	1.1
Minor elements (cations)						
Calcium	75,700	0.46	0.48	0.30	0.27	0.26
Iron	146,600	1.5	1.7	0.97	0.89	0.77
Sulfur	218,900	0.007	0.020	-	0.027	-
Anions						
Chloride	1,010	0.086	0.050	2.1	0.035	0.59
Fluoride	776	0.014	0.054	0.80	0.038	0.86
Nitrate	58.2	0.27	0.47	3.1	0.59	1.5
Sulfate	27,650	0.024	0.25	0.25	0.10	0.20

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[a] Coal ash = $\frac{\text{ppm in coal}}{\text{fraction ash content in coal}}$

SECTION IX

DISCUSSION OF RESULTS

This section presents more extensive discussion of key results from the Widows Creek test program.

MASS BALANCE

The primary indicator of the reliability of test results obtained in this study is overall mass balance. The average and the range of mass imbalance for each pollutant are given in Table 41 (second column).

With the exception of cadmium and manganese, the precision of measured mass balance is within the expected tolerance (Table 42) based on the statistical model described earlier (Table 11). Additional statistical analysis (using techniques described in Appendix D) indicates that the primary sources of mass balance imprecision are analytical imprecision and nonrepresentative sampling.

As indicated in the last two columns of Table 41, nonrepresentative sampling accounts for most of the mass balance imprecision observed. This is apparently due to the nonuniformities of elemental concentrations in the bulk ash streams. Physical evidence to support this is the wide range of color and texture observed for the bottom ash and superheater ash samples collected at different times.

Of greater importance is the average degree of mass imbalance (i.e., inaccuracy in mass balance) for each pollutant. The two major causes of statistically significant mass imbalances (exceeding $|\pm 25\%|$) are inefficient collection of vaporous elements (resulting in highly negative imbalance) and analytical error.

Table 41. PRINCIPAL SOURCES OF INACCURACY AND IMPRECISION IN MASS BALANCE

Pollutant	Overall Mass Imbalance (%)	Sources of Inaccuracy[a] Inefficient Pollutant Collection	Sources of Inaccuracy[a] Analytical Error	Sources of Imprecision (percentage contribution) Analytical Imprecision	Sources of Imprecision (percentage contribution) Nonrepresentative Sampling
Trace Elements (cations)					
Antimony	- 72 ± 6	X		3.0	97.0
Arsenic	- 94 ± 1	X			
Barium	+ 73 ± 17		X[c]	40.6	59.4
Beryllium	- 18 ± 15			2.8	97.2
Cadmium	- 46 ± 34	X		1.7	98.3
Chromium	4 ± 9			24.0	76.0
Cobalt	- 47 ± 21		X	4.1	95.9
Copper	- 12 ± 15			15.0	85.0
Lead	- 25 ± 21			4.4	95.6
Manganese	6 ± 29			3.3	96.7
Mercury	- 63 ± 20[b]	X		0.3	99.7
Nickel	- 5 ± 16			24.3	75.7
Selenium	- 76 ± 9	X		1.5	98.5
Tellurium	- 68 ± 3		X[c]	12.8	87.2
Tin	- 80 ± 2		X[c]	8.8	91.2
Titanium	6 ± 22			7.1	92.9
Vanadium	- 14 ± 22			1.9	98.1
Zinc	- 47 ± 5[b]		X	0.3	99.7
Minor Elements (cations)					
Calcium	- 61 ± 19		X	1.4	98.6
Iron	22 ± 25			6.7	93.3
Sulfur	- 15 ± 10				
Anions					
Chloride	- 79 ± 5[b]	X			
Fluoride	- 74 ± 6	X			

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a/ Average overall mass imbalance exceeding ± 30%.

b/ Based on two runs only.

c/ Near the limit of detection of the analytical method.

Table 42. MASS IMBALANCE VERSUS SAMPLING FREQUENCY

Tolerance d(%)[a]	Number of samples per run (all streams)		
	90% Confidence Level	95% Confidence Level	99% Confidence Level
5	59	83	143
10	15	21	36
15	7	10	16
20	4	6	9
25	3	4	6
30	2	3	4
40	1	2	3
50	1	1	2

---

a/ Expected range of mass imbalance for nonvolatile elements.

Inefficient pollutant collection accounts for the highly negative imbalance observed for antimony, arsenic, mercury, selenium, and fluorine. For the other six elements for which mass imbalance was significant, analytical errors are thought to be important, although the data on analytical accuracy (Table 30) are not extensive enough to quantitate this dependence. For cobalt, tin, zinc, and chlorine, inconsistencies in stream enrichment (Table 40) support the probability of systematic analytical errors. Measured levels of tellurium and tin were near the detection limits.

MODIFICATIONS TO SAMPLING TRAIN

To improve the efficiency of collection of vaporous elements from the flue gases, modifications to the sampling train are recommended. The modified sampling train (Figure 33) has the following basic features:

1. Pyrex-lined probe (or stainless if longer than 8 ft) heated to stack temperature.

2. Quartz fiber filter, heated to stack temperature, for collection of particulates; filter preceded by stainless cyclone if high grain loading.

3. Eight impingers in an ice-water bath for collection of condensibles and inorganic vaporous species: first two impingers, saturated sodium carbonate (for removal of condensed moisture, sulfur dioxide, condensed organics, selenium and antimony); third impinger, dry (for removal of carry-over from second impinger); fourth and fifth impingers, acid dichromate (for removal of inorganic vapors); sixth impinger, acid permanganate (for removal of inorganic vapors); seventh impinger, dry (for removal of carry-over from sixth impinger); and eighth impinger, silica gel (for removal of residual water vapoor).

4. Quartz filter (optional) at 50 to 60°F between third and fourth impingers for collection of condensed particulate.

5. Tenax-GC® plug for collection of organic vapors.

6. Gas meters and pump as prescribed by EPA Method 5.

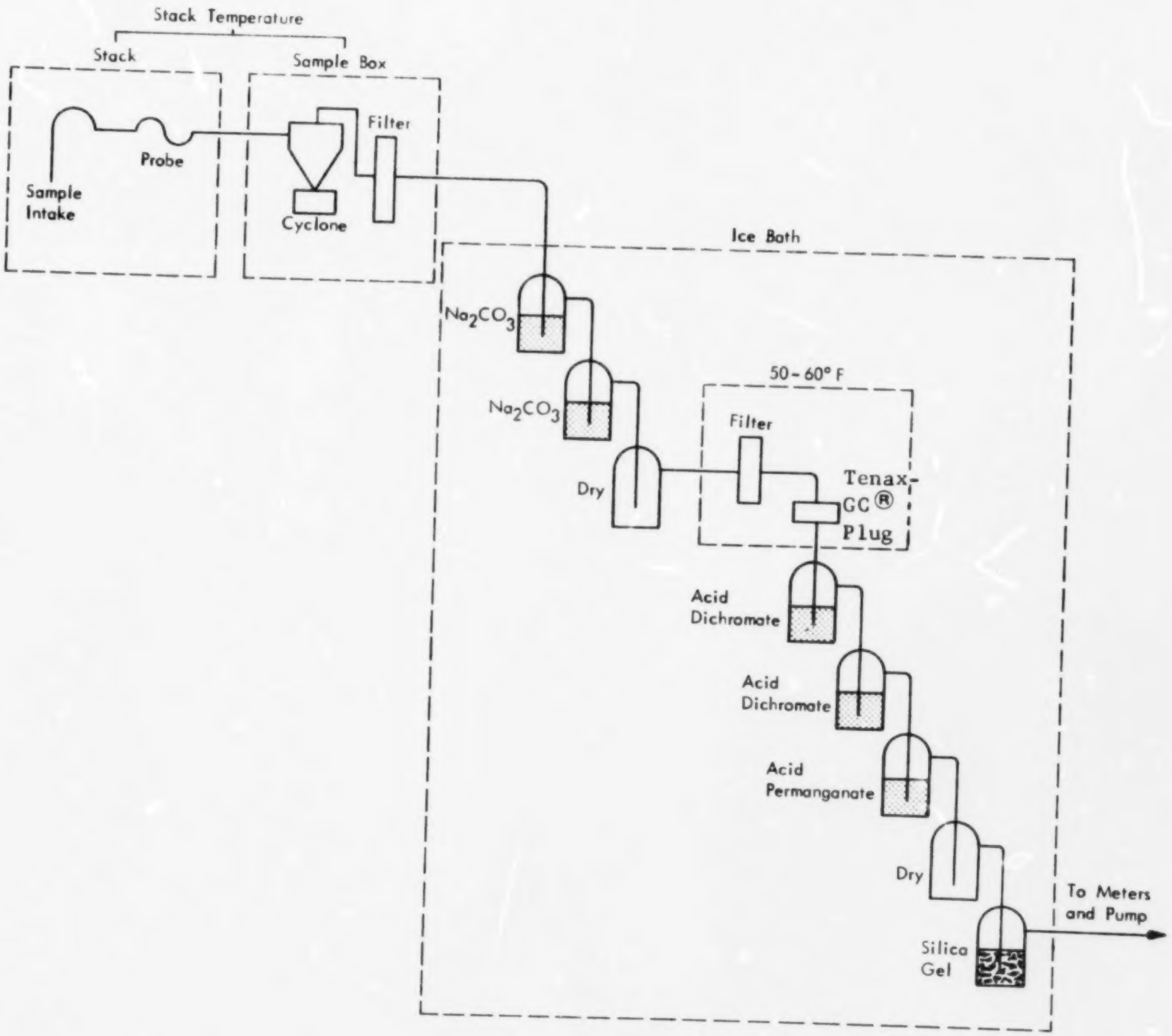

Stack Temperature
Stack
Sample Box
Sample Intake
Probe
Cyclone
Filter
Ice Bath
Na_2CO_3
Na_2CO_3
Dry
50 - 60° F
Filter
Tenax-GC® Plug
Acid Dichromate
Acid Dichromate
Acid Permanganate
Dry
Silica Gel
To Meters and Pump

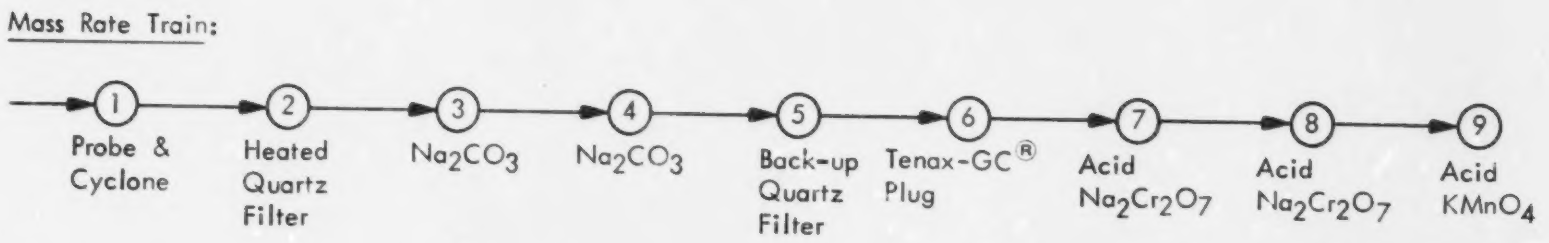
Figure 33. Modified flue gas sampling train.

The analyses to be performed on each component of the modified sampling train are indicated in Figure 34. Procedures to be used for removing collected samples from the train are identical to those described in Section V, with the exception that nitric acid-potassium dichromate is suggested for rinsing the acid-solution impingers. A schematic of sample treatment and analysis steps is shown in Figure 35. The recommended analytical techniques are those used in the Widows Creek Study.

HEALTH HAZARD EVALUATION

Table 43 presents an approximate evaluation of the potential health hazard associated with the ground-level concentrations of pollutants resulting from the emissions of toxic elements in boiler flue gases. The "worst case" concentrations are based on the assumption that all of the element in coal is emitted with the stack gases. These concentrations are more realistic than the measured concentrations for the vaporous elements.

The health hazard assessment is made by comparing the maximum ground-level concentration with the corresponding threshold limit value (TLV).[33/] A factor of 10^3 is used to account for stack gas dilution between the point of emission and the maximum ground-level receptor point. Because the threshold limit value specifies the concentration to which a person may be safely exposed during a normal 40-hr work week, this value should be reduced by at least a factor of 10 if it is to be applied to continuous exposure situations. With this taken into account, only beryllium concentration is near the level of potential concern.


Mass Rate Train:
1
Probe & Cyclone
2
Heated Quartz Filter
3
Na_2CO_3
4
Na_2CO_3
5
Back-up Quartz Filter
6
Tenax-GC®
Plug
7
Acid
$Na_2Cr_2O_7$
8
Acid
$Na_2Cr_2O_7$
9
Acid
$KMnO_4$

Analysis \ Sample	1	2	3	4	5	6	7	8	9
Elemental	●	●							
POM, PCB	●	●	●	●	●	●			
Sulfates, Nitrates	●	●	●	●					
Se, As, Sb, Hg	●	●	●	●			●	●	●
Particulates	●	●							

Figure 34. Required analyses for mass-rate train.

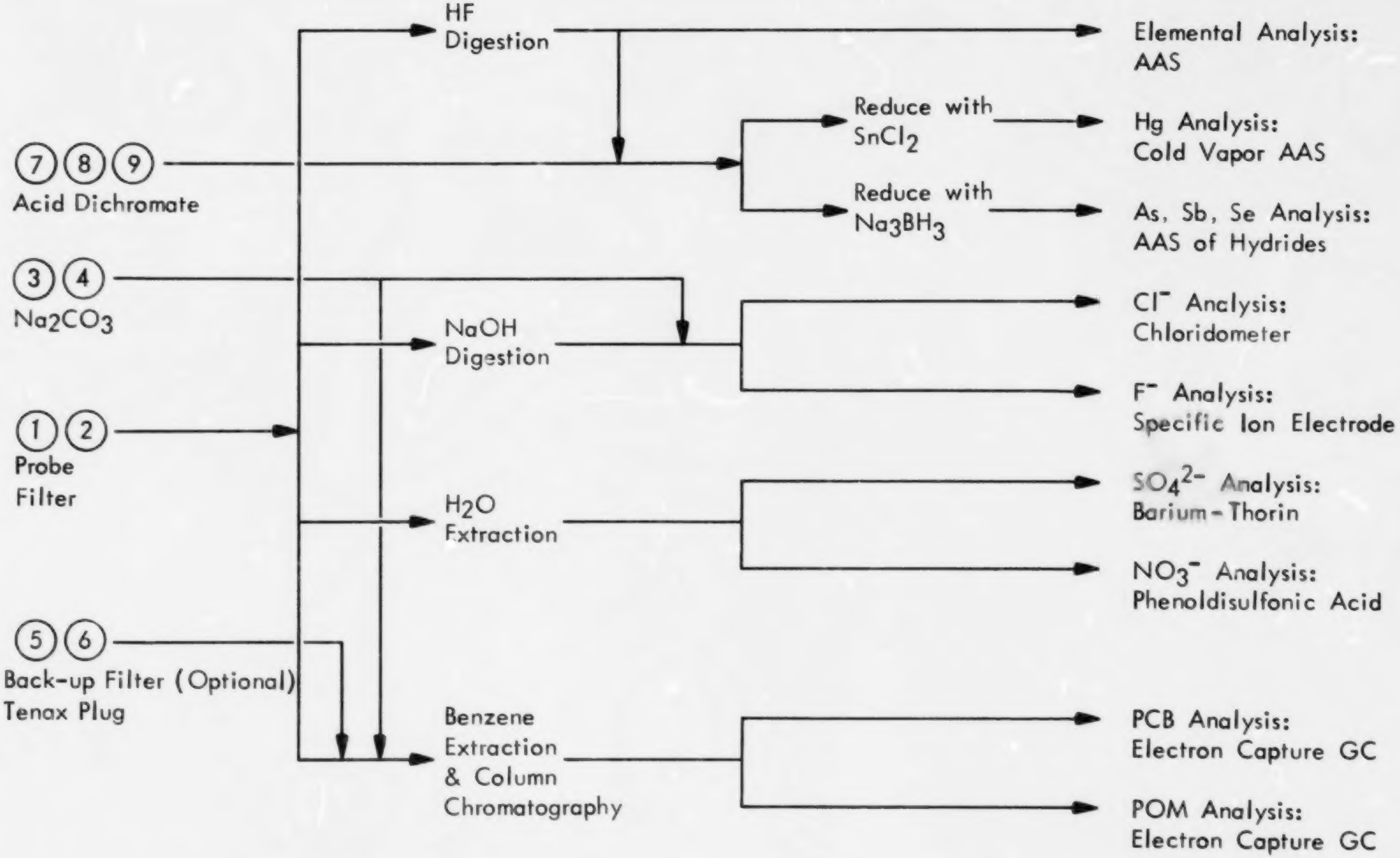

⑦⑧⑨ Acid Dichromate
③④ Na_2CO_3
①② Probe Filter
⑤⑥ Back-up Filter (Optional) Tenax Plug
HF Digestion
NaOH Digestion
H_2O Extraction
Benzene Extraction & Column Chromatography
Reduce with $SnCl_2$
Reduce with Na_3BH_3
Elemental Analysis: AAS
Hg Analysis: Cold Vapor AAS
As, Sb, Se Analysis: AAS of Hydrides
Cl^- Analysis: Chloridometer
F^- Analysis: Specific Ion Electrode
SO_4^{2-} Analysis: Barium-Thorin
NO_3^- Analysis: Phenoldisulfonic Acid
PCB Analysis: Electron Capture GC
POM Analysis: Electron Capture GC

Figure 35. Sample preparation and analysis diagram.

Table 43. POTENTIAL HEALTH HAZARD EVALUATION--AVERAGE ALL RUNS

Pollutant	Concentration in coal (ppm)	Concentration in flue gases (mg/m^3) Dust collector inlet	Concentration in flue gases (mg/m^3) Dust collector outlet	Concentration in flue gases (mg/m^3) Worst case[a]	Worst case ground level concentration (mg/m^3)	Threshold limit value (mg/m^3)
Trace elements (cations)						
Antimony	< 1.1	< 0.00464	0.00347	0.060	0.000060	0.5
Arsenic	14.3	0.0404	0.0203	0.806	0.00081	0.5
Barium	< 168	4.26	2.50	9.49	0.0095	0.5
Beryllium	1.5	0.0387	0.0221	0.084	0.000084	0.002
Cadmium	0.99	0.032	0.020	0.0558	0.000056	0.1-0.2
Chromium	24	0.983	0.514	1.33	0.0013	0.5-1.0
Cobalt	1.45	0.028	0.009	0.0806	0.000081	0.1
Copper	10	0.327	0.175	0.579	0.00058	1
Lead	3.72	0.158	0.091	0.211	0.00021	0.15-0.2
Manganese	35	1.22	0.490	1.99	0.0020	5-6
Mercury	1.91	0.0938	0.0421	0.107	0.00011	0.05
Nickel	15	0.640	0.293	0.861	0.00086	1
Selenium	< 6.1	0.128	< 0.0399	0.339	0.00034	0.2
Tellurium	< 30	< 0.146	< 0.0772	1.69	0.0017	0.1
Tin	1.69	0.013	0.0045	0.0949	0.000095	2
Titanium	895	30.9	16.2	50.0	0.050	10-15
Vanadium	62	1.68	1.02	3.48	0.0035	0.1-0.5
Zinc	55	1.77	0.934	3.15	0.0032	5
Minor elements (cations)						
Calcium	12,000	114	49	677	0.68	-
Iron	23,200	686	268	1,310	1.31	-
Anions						
Chloride	152	10.5	1.39	8.33	0.0083	3
Fluoride	121	2.99	1.58	6.77	0.0068	2.5
Nitrate	9.1	0.837	0.198	0.513	0.00051	-
Sulfate	-	33.9	13.3	-	-	-

---

[a] Worst case = $\frac{\text{Pollutant mass flow rate in coal (gm/min)}}{\text{Average dust collector outlet flow rate (acfm)}} \times 35.3$

APPENDIX A

PROCEDURES FOR HANDLING, PREPARATION AND ANALYSIS OF SAMPLES

This appendix describes the procedures used to treat samples collected in the Widows Creek test program. The procedures fall into four categories:

1. Removal of samples from the collection apparatus.

2. Storage of samples.

3. Preparation of samples for chemical analysis.

4. Chemical analysis of samples for pollutant content.

COAL AND ASH SAMPLES

Composition Procedures

Samples of coal, superheater ash, and dust collector ash were composited for each run. Each composite sample (~ 20 g) was prepared by weighing equal quantities of the individual samples of coal or ash from a given run. Composite samples were mixed thoroughly prior to chemical analysis. If additional composite samples were required, analytical comparisons were made to ensure equivalence.

Because bottom ash samples consisted of a slurry of highly nonuniform aggregate in sluice water, composite samples could not be prepared by the technique described above. After the wet-bottom ash samples from each run were combined, the sluice water was decanted off and the separated ash was air dried. Finally, the total dried bottom ash from a given run was ground in a ceramic-ball mill to less than 120 mesh.

Analysis for Trace Metals

Sample Preparation - Two samples of coal and each type of ash for each run were obtained from representative portions of the composite sample. At least five portions were taken from different parts of the composite sample until the approximate desired sample weight (~ 100 mg) is obtained.

Two portions of each type of solid sample from each run were analyzed. The first portion of each sample type from one run was analyzed directly; the second portion of each type from that run was fortified with 1 ml of nitric acid solution containing approximately the same mass of each of the 20 metals as expected in the sample so that quantitative recoveries could checked. The sets of duplicate samples of each type from the remaining runs were digested and analyzed identically to check the precision of the analytical methods.

The procedure for digestion of samples was as follows. After each sample is accurately weighed into a Teflon cup, it was placed in a Parr digestion bomb with 3 ml of 48% HF added. The bomb was sealed and digested at 130°C for approximately 12 hr. After time was allowed for cooling to room temperature, 1.5 g of boric acid was added and the solution was diluted to 25 ml. If the coal samples had not undergone total dissolution, they were centrifuged and the solution decanted off for analysis. The undissolved material remaining was again digested with HF. Analyses of these redigested samples indicated very little metal remaining after the first digestion.

Sample Analysis - The digested material was analyzed by atomic absorption spectrophotometry. Four different methods of atomic absorption were used--conventional flame methods, carbon rod atomization (or micro flameless methods), metal hydride generation with nitrogen entrained-air hydrogen flame, and cold vapor. Table 13 indicated the particular AAS technique used to quantitatively determine the concentration of each trace metal present in the samples. In each case, the selection of the atomic absorption technique was based on the expected concentration of the metal and the sensitivities of the various AAS techniques.

Mercury was determined by cold vapor AAS. An aliquot of the digested solution was placed in 20 ml of water and prereduced with hydroxylamine hydrochloride. Stannous chloride was then added to reduce Hg^{+2} to Hg^0 and the Hg^0 was swept into a cold vapor atomic absorption cell with nitrogen.

Arsenic, antimony, and selenium were converted to their respective volatile hydrides prior to AAS analysis. This was done by placing an aliquot into a 25% HCl solution, sealing the solution in a screw-cap jar and rapidly adding 5 ml sodium borohydride. The respective volatile hydrides that were formed were swept out of the cell with nitrogen into a hydrogen flame. The concentration was then determined by atomic absorption at the appropriate wavelength for each element.

In order to determine if the conventional flame atomic absorption methods were sufficiently sensitive for the remaining 16 metals, coal samples were analyzed using air acetylene or nitrous oxide-acetylene flames. Coal samples were selected for this test because the various metal concentrations are lower in coal than in any other type of sample. The concentrations were determined for each metal using composite standards containing all 20 metals of interest and the same concentrations of hydrofluoric acid and boric acid as the sample.

The trace metals that were below the detection limit for flame atomic absorption were determined by carbon rod atomization. The hydrofluoric acid used to digest the solid samples and the boric acid added after digestion was a previously untested matrix for the carbon rod technique. MRI has done extensive development work to assure that this matrix is compatible for analysis by this technique. We have found that it is a workable matrix if care is taken in the experimental procedure.

Each element was optimized for maximum sensitivity and minimum background interference before the sample was analyzed. Background and standards were checked frequently to assure minimum interference. Several metals that were analyzed by flame methods were checked by the carbon rod technique to determine the agreement between the two techniques.

Analysis for Anions

Sample Preparation for Chloride and Fluoride - Blended duplicate samples (1 g quantities) of each type were subjected to high-pressure digestion. After addition of mineral oil to accurately weighed samples, the samples were sealed in bombs, pressurized with oxygen, and combusted. The chloride and fluoride were trapped in 1 N sodium hydroxide, neutralized, brought to volume, and split for chloride and fluoride analysis.

Sample Analysis for Chloride and Fluoride - Chloride analyses were done with a chloridometer which coulometrically generates Ag^+ ions at a constant rate. The end point was detected amperometrically. Concentrations were found from calibration of chloride concentration versus time of Ag^+ generation.

Fluoride concentrations were determined potentiometrically with a fluoride selective electrode. The neutralized samples were mixed 1:1 with total ionic strength buffer solution. A linear calibration of the log of fluoride concentration versus millivolt response was obtained for standards from 0.05 to 100 ppm. Samples above 100 ppm were diluted to bring them into the linear range.

Sample Preparation for Sulfate and Nitrate - The solid samples were accurately weighed to 5 g and Soxhlet extracted for 24 hr with water. It should be noted that with solid samples only water soluble sulfate and nitrate were determined.

Sample Analysis for Sulfate and Nitrate - Sulfate concentration was determined by barium titration to the thorin end point; and nitrate determinations were made spectrophotometrically using the phenoldisulfonic acid method. These two procedures were the same as specified in the Federal Register for SO_2 and NO_x determinations.[28]

Analysis of Organics

Two classes of organic compounds were of interest in this study, polycyclic organic materials (POM) and polychlorinated biphenyls (PCB). Eight POM compounds with the highest carcinogenicity, were screened for identification and quantitative analysis.

Sample Preparation for PCB and POM - Duplicate samples (5 g each) of coal and each type of ash were Soxhlet extracted for 24 hr with benzene. One of the two samples from one run was spiked with Aroclor-1260 and benzo[a]pyrene before extraction to check recovery of the sample during the preparation and analysis procedure. All benzene extracts were evaporated to dryness and redissolved in a known volume of benzene.

Sample Analysis for PCB and POM - PCB samples were analyzed on a gas chromatograph equipped with a tritium electron-capture detector. A 6-ft x 1/4-in. glass column packed with 1.5% OV-17 and 1.95% QF-1 on 100/120 mesh Gas Chrom Q was used. Aroclor-1260, tetrachlorobiphenyl and hexachlorobiphenyl were used as standards. Seven of the major peaks from Arochlor-1260 were used for retention time matching with the samples. The concentration of identified PCB compounds were calculated on the basis of the Aroclor standards. Additional identifications were made on a second column using OV-1, and GC/MS verification of the higher concentration samples was attempted.

Analysis of POM compounds was made on a gas chromatograph equipped with a flame ionization detector. A 6-ft x 1/4-in. glass column packed with 3% Dexsil 300 on Supelcoport was used. Only five of the eight POM compounds of interest could be obtained as standards, at the time of this study, i.e., 7,12-dimethylbenz[a]anthracene, benzo[a]pyrene, 3-methylcholanthrene, dibenz[a,h]anthracene and dibenzo[a,i]pyrene. The possible presence in these samples of the other three POM of interest (benzo[c]phenanthrene, dibenzo[a,i]pyrene, and dibenzo[C,g]carbazole) was checked by relative retention time matching from other investigations.[29a]

Proximate and Ultimate Analysis

Proximate and ultimate analyses were performed on the coal samples and proximate analysis on the bottom ash, superheater ash, and dust collector ash samples.

FLUE GAS SAMPLES

Hazardous Pollutants

A summary of the analyses that were performed on discrete samples obtained from various components of the hazardous pollutant sampling train was shown earlier (Figure 14). The overall sample preparation and analysis system was diagrammed in Figure A-1.

The following paragraphs discuss the sample handling and preparation procedures that were applied to each component of the sampling train. The analysis procedures are identical to those described for coal and ash samples in the preceding sections.

Sample Handling

The procedures used for removing collected samples from the sampling train were as follows:

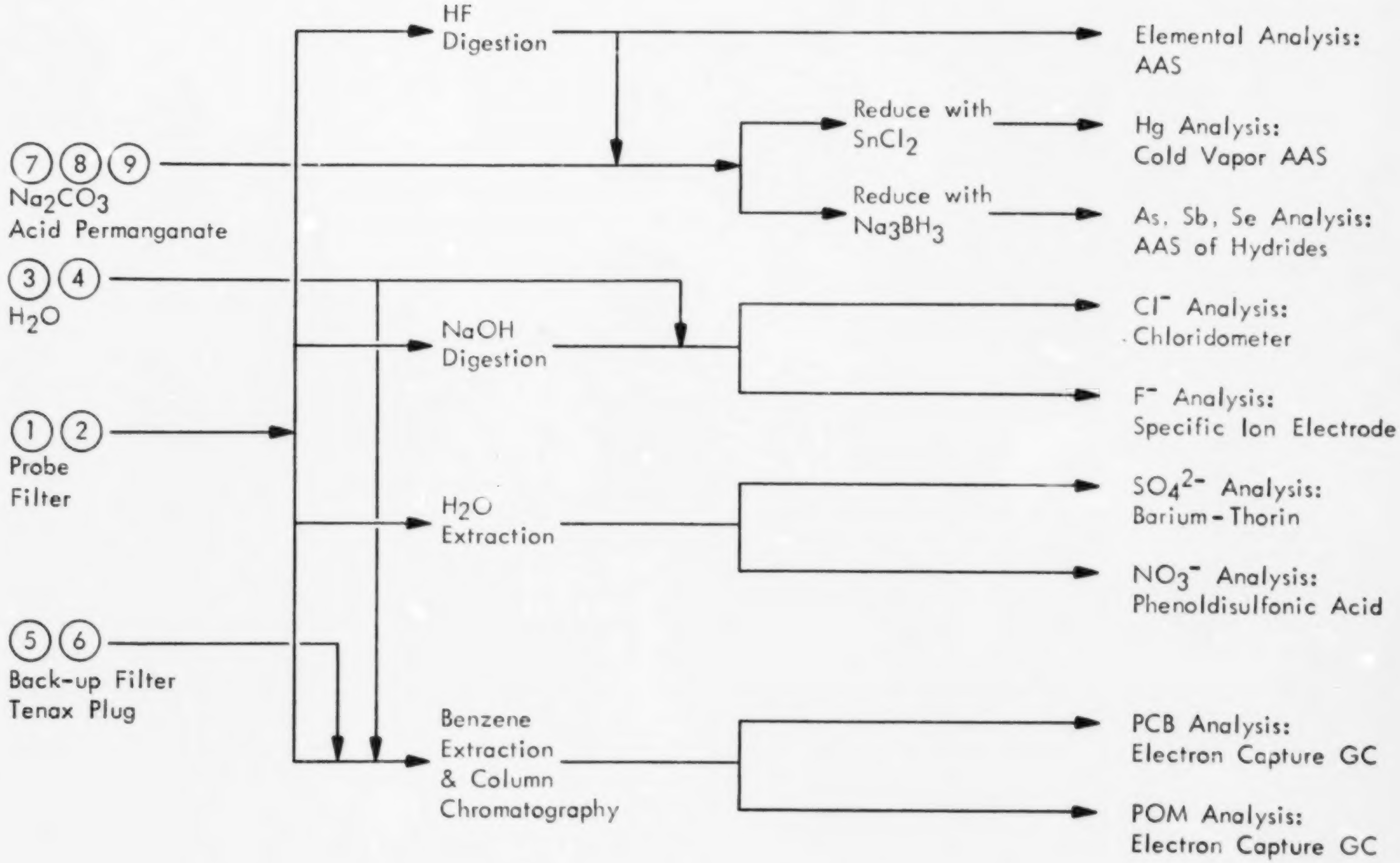

⑦⑧⑨ Na_2CO_3 Acid Permanganate
③④ H_2O
①② Probe Filter
⑤⑥ Back-up Filter Tenax Plug
HF Digestion
NaOH Digestion
H_2O Extraction
Benzene Extraction & Column Chromatography
Reduce with $SnCl_2$
Reduce with Na_3BH_3
Elemental Analysis: AAS
Hg Analysis: Cold Vapor AAS
As, Sb, Se Analysis: AAS of Hydrides
Cl^- Analysis: Chloridometer
F^- Analysis: Specific Ion Electrode
SO_4^{2-} Analysis: Barium-Thorin
NO_3^- Analysis: Phenoldisulfonic Acid
PCB Analysis: Electron Capture GC
POM Analysis: Electron Capture GC

Figure A-1. Sample preparation and analysis diagram.

- The probe tip and probe were rinsed with minimum quantities of acetone and chloroform and the rinses combined in a screw-cap (Teflon) glass bottle.

- The heated quartz filter was removed from the holder and placed in a wide-mouth screw-cap jar.

- The water impinger solutions were transferred to a screw-cap bottle; the impingers were rinsed with acetone and the rinses transferred to a separate screw-cap bottle.

- The backup filter and the Tenax-GC® were placed in separate wide-mouth screw-cap jars.

- The sodium carbonate impinger solution was transferred to a screw-cap (Teflon) glass bottle.

- The acid permanganate absorbing solutions were transferred into separate bottles. Each impinger was rinsed with a nitric acid-potassium dichromate solution and the rinses combined with the respective absorbing solution.

- A minimum quantity of 3% hydrogen peroxide solution was used to dissolve residues on the acid-permanganate impingers. This rinse was transferred to a screw-cap glass bottle.

- The final (dry) impinger was rinsed with 3% hydrogen peroxide solution to analyze for additional catch (if any). This rinse was transferred to a separate screw-cap glass bottle.

- The silica gel was transferred to a wide-mouth screw-cap bottle.

All glassware used to store and/or transport components of the sampling train was precleaned by washing with detergent, rinsing with tap water, soaking in warm acid, rinsing with distilled water, and rinsing with acetone.

Sample Preparation

The procedures used to prepare for analysis the samples removed from each component of the sampling train are described below.

Probe ① - The probe tip and probe rinse (acetone/chloroform) was evaporated to dryness and the residue weighed for particulate loading. The residue was split into five parts, which are treated as follows: a 1-g portion was digested (as described in the coal and ash section) for chloride and fluoride analysis; the second 1-g portion was extracted with benzene for organic analysis; two portions were hydrofluoric acid digested for metals analysis, and the final portion was water extracted for sulfate and nitrate analysis.

First Filter ② - The quartz filter and loose catch was desiccated and weighed for particulate determination and then the loose catch was divided into four portions that were treated as described immediately above.

Water Impingers ③ and ④ - The water impinger solutions were extracted with benzene for organic anlaysis; the three portions of benzene used in the extraction were combined, evaporated to dryness, and the residue redissolved in a known volume of benzene. Each impinger was treated as a separate sample to evaluate trapping efficiency. Aliquots were taken from the aqueous portion of the first impinger solution for chloride, fluoride, sulfate and nitrate analysis (after pH adjustment). The remaining aqueous solution was then evaporated and the residue weight taken for the particulate determination.

Second Filter ⑤ - The second quartz filter was desiccated and weighed for particulate loading determination. The filter was then benzene extracted and analyzed for POM and PCB.

Tenax-GC® ⑥ - The Tenax-GC® was mixed with benzene, sonified, and centrifuged. The benzene was decanted off and analyzed for POM and PCB.

Na_2CO_3 ⑦ and Acid Permanganate Impingers ⑧ and ⑨ - These impinger solutions were digested with acid permanganate and each brought to 100 ml volume. They were then analyzed for mercury, antimony, selenium, and arsenic.

Particle Size Samples

Each portion of sample obtained in the Brink cascade impactor, i.e., a cyclone catch, five impactor stages (each with a distinct particle size cutoff diameter), and a tissue-quartz backup filter, was analyzed for cationic elements. Due to insufficient sample quantities anticipated, analyses for organics, sulfate, nitrate, chlorides and fluorides were not made.

Sample Handling

After a sizing test, the aluminum foil liners were transferred to snap-cap plastic vials.

Sample Preparation - The combined Brink samples were washed and sonified with acetone into Teflon Parr bomb digestion cups. The Teflon cups were weighed before digestion and after the digested sample has been removed. The backup filters were digested with the filter catch to avoid removal of the catch from the quartz filter. The digestion procedure were modified to account for the small ash weights by using proportionally less hydrofluoric acid, boric acid, and a smaller final sample volume.

Sample Analysis - Trace metals were analyzed by carbon rod atomization atomic absorption because of the small sample volumes (1 to 10 ml) and the desire to analyze for 21 metals (including thallium). The reproducibility and background absorption was carefully checked for each of the trace metals. The various carbon rod atomizer operating parameters for each metal determined were optimized for a maximum absorption signal and a minimum background interference as checked by hydrogen lamp.

SO_2, NO_x, and Carrier Gases - EPA Methods 6, 7, and 3 were followed in the analysis of collected flue gas samples for sulfur dioxide, nitrogen oxides, and dry carrier gases, respectively. SO_2 concentration was determined by barium titration of the appropriate absorbing solution to the thorin end point; NO_x concentration by spectrophotometric analysis of the appropriate absorbing solution using the phenoldisulfonic acid method; and dry gas composition by the Orsat technique.

Inlet Air

The Tissuquartz filters from the high-volume samplers were conditioned and weighed to determine the particulate loading in the sampled inlet air.

APPENDIX B

REVIEW OF CHEMICAL ANALYSIS METHODOLOGY

This appendix presents a review of chemical analysis methods which are applicable to the determination of hazardous constituents in utility boiler flue gases. Following a general review of candidate analysis methods, details are presented on the methods of choice for each pollutant category. This is followed by a brief description of alternate methods of analysis.

CANDIDATE ANALYSIS METHODS

Generally, it is not feasible to select one analytical method that is superior to all others for the analysis of a group of elements or compounds. Each method has areas of strength and weakness when compared to other methods. The selection of any method is based on many factors including the following: accepted performance criteria, e.g., accuracy, precision and detection limits; cost-time factors; and the degree of sophistication and reliability of the required instrumentation. In addition, the effect of the bulk matrix composition of "real world" samples on each of the above criteria must be considered.

General Approach

The quantity of sample available at certain sampling stations is limited. For example, the effluent gases sampled at the outlet of electrostatic precipitators have relatively low concentrations of particulates (~ 0.1 gr/scf). Increased quantities of particulates can be collected by extending the sampling time, but sampling times are also limited by practical considerations such as crew exposure, cost and durability of equipment. Because of possible sample size limitation, the strategy for selecting analytical methods is based on choosing analysis procedures that are most compatible with a common sample preparation method which can be applied to a large group of pollutants.

The hazardous pollutants can be divided into two major groups: organic compounds (polynuclear organic materials and polychlorinated biphenyls) and elemental inorganic compounds. The latter group can be subdivided into those elements which form anions (chlorides and fluorides) and those which form cations upon sample dissolution. A general procedure for dividing the sample into these three groups is depicted in Figure B-1. The organic compounds are removed from the sample by extraction with benzene. Compounds of special interest, e.g., the highly carcinogenic benzo[*a*]pyrene and polychlorinated biphenyl are highly soluble in benzene whereas elemental pollutants are insoluble

5

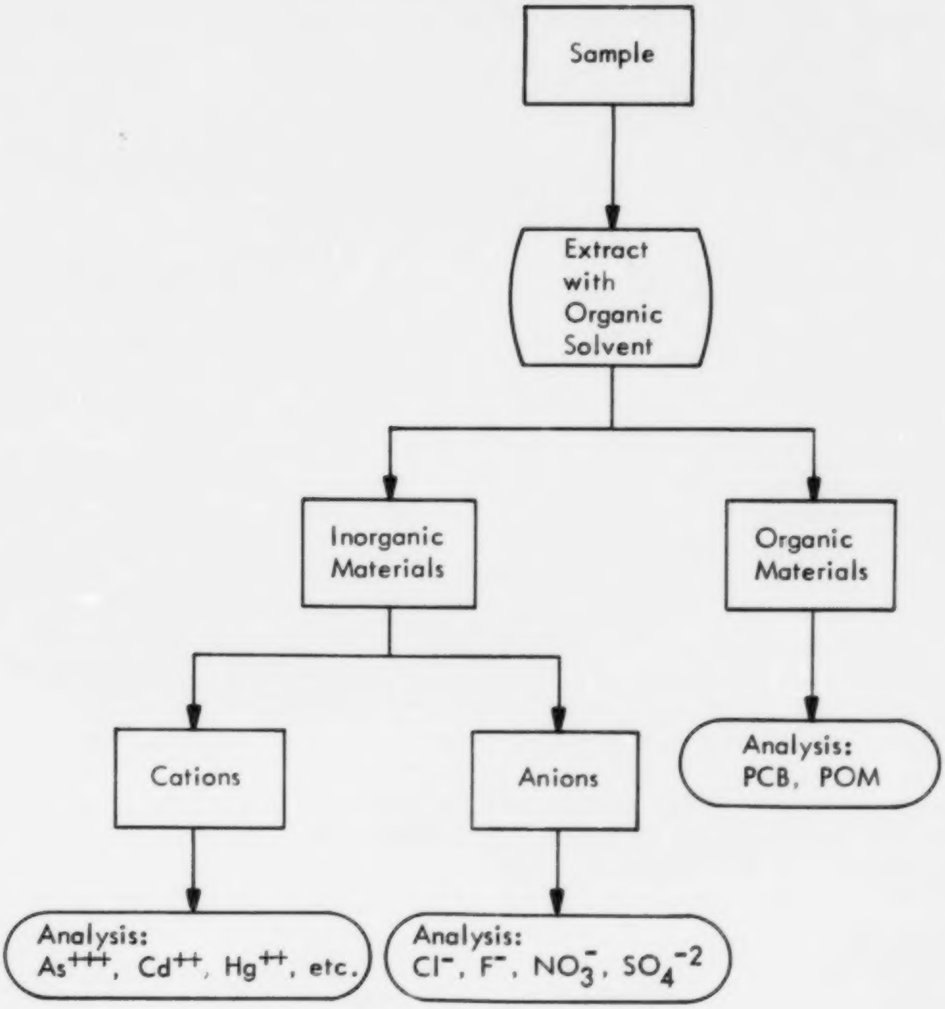

Sample
Extract with Organic Solvent
Inorganic Materials
Organic Materials
Cations
Anions
Analysis: PCB, POM
Analysis: As^{+++}, Cd^{++}, Hg^{++}, etc.
Analysis: Cl^-, F^-, NO_3^-, SO_4^{-2}

Figure B-1. General procedure for sample treatment and analysis.

in benzene except when present as organometallic complexes, which have limited solubility in benzene. The loss of inorganic pollutants, if any, can be determined by elemental analysis of a number of benzene extracts; it is not expected to be significant. The benzene insoluble material is divided and analyzed for cationic and anionic pollutants.

The analysis methods that can be applied to elemental and organic pollutants are discussed in the following paragraphs.

Elemental Analysis

A number of methods have been applied to the analysis of cationic elements[3,7,13,18, 34] including:

- Atomic absorption (AA) and emission spectrometry;
- Neutron activation analysis (NAA);
- X-ray fluorescence spectrometry (XFS);
- Spark source mass spectrometry (SSMS); and
- Electrochemical methods (EC--voltametry and potentiometry).

The feasibility of analyzing each of the elemental pollutants of interest by the methods mentioned in the preceding paragraph is indicated in Table B-1. A plus indicates the analysis is feasible; a minus indicates the analysis is not feasible; and a circled plus indicates MRI has the capability of performing the analysis in-house. The criteria used to determine the feasibility of each analysis were:

1. Detection limits: The detection limit of the method for coal and fly ash matrices was considered versus the expected concentration of the element. If the detection limit was above the expected concentration, the method was indicated as not feasible.

2. Sample requirements: If a method required a prohibitive sample size (> 1.0 g of particulate) or large dilution factors for multielement analysis, it was indicated as not feasible.

3. Accuracy and precision: The accuracy and precision of the method must be sufficient to obtain a meaningful material balance for the element in question. A relative standard deviation of ± 20% was selected arbitrarily. Each of the methods indicated as acceptable meet this requirement in the most extreme situation (i.e., near a signal level of

Table B-1. FEASIBILITY OF ANALYTICAL METHODS[a]

Elemental Pollutant	AA	AA (micro)	NAA[b]	XRF	OES[c]	EC[d]
Antimony	⊕ e/	⊕	+	-	+	⊕
Arsenic	⊕ e/	⊕	+	-	+	⊕
Barium	⊕	-	+	⊕	+	-
Beryllium	⊕	⊕	-	-	+	-
Cadmium	-	⊕	+	-	-	⊕
Chromium	⊕	⊕	+	-	+	⊕
Cobalt	⊕	⊕	+	-	+	⊕
Copper	⊕	⊕	+	-	+	⊕
Lead	⊕	⊕	-	-	+	⊕
Manganese	⊕	⊕	+	⊕	+	⊕
Mercury	⊕ f/	⊕	+	-	+	-
Nickel	⊕	⊕	+	⊕	+	⊕
Selenium	⊕ e/	⊕	+	-	-	-
Tellurium	⊕ e/	⊕	+	-	+	-
Thallium	⊕	⊕	+	-	+	-
Tin	-	⊕	+	-	+	-
Titanium	⊕	⊕	+	⊕	+	-
Vanadium	-	⊕	+	⊕	+	-
Zinc	⊕	⊕	+	-	+	⊕
Chlorine	-	-	+	⊕	-	⊕
Fluorine	-	-	+	-	-	⊕

---

a/ The analytical procedures are as follows: AA, atomic absorption spectrophotometry; AA (micro), AA with carbon rod or other flameless atomization; NAA, neutron activation analysis; XRF, X-ray fluorescence spectrometry; OES, optical emission spectrometry; EC, electrochemical methods.

b/ NAA methods include chemical pretreatment.

c/ OES methods include chemical pretreatment, photometric detection, DC arc (inert atmosphere) and argon plasma sources.

d/ EC methods are anodic stripping voltametry and potentiometry (specific ion electrode for fluoride).

e/ Includes SbH_2, AsH_3, and SeH_3 generation and N_2-H_2-air flame.

f/ Cold vapor.

twice the noise level). At normal working levels, the feasible methods generally are within a relative standard deviation of 5%. Because of these criteria, SSMS is not listed in Table B-1. The NAA and OES ratings are for methods which include chemical pretreatment. The OES methods are DC Arc (controlled atmosphere) or argon induction coupled plasma methods with photometric detection and not routine survey methods.

Cost considerations are not reflected in Table B-1. Because several chemical treatment procedures are required for NAA and OES analysis of 20 elements of interest, these methods are more costly than AA analysis. A realistic cost for AA analysis, including man-hours, chemicals and instrument operation and upkeep, is approximately \$10/sample for sample preparation plus \$5 to \$10/element quantified. To achieve comparable sensitivity, accuracy and precision, the cost for sample preparation(s) prior to NAA and OES analysis is on the order of \$50/sample. The costs for electrochemical analyses are similar to AA where satisfactory methods do exist.

Other anionic pollutants of interest, in addition to elemental anionic pollutants, include sulfates and nitrates. A variety of methods have been applied to the detection of both sulfates and nitrates. Spectrophotometric methods are most successful for the analysis of nitrate. Particulate sulfate analysis methods are the subject of a recent review by Forrest and Newman.[35] Included in this review are turbidimetric, photometric electrochemical, microtitration X-ray emission, and other methods.

Analysis of Organic Materials

Gas chromatography, liquid chromatography, and UV-visible spectroscopy have been applied to the analysis of POM and PCB.[36-39] Identification of both types of organic compounds should be verified by mass spectrometry if sufficient concentrations are present. Verification is accomplished most conveniently by a mass spectrometer interfaced directly with a gas chromatograph.

ANALYSIS METHODS OF CHOICE

Table B-2 indicates the methods of chemical analysis that are recommended for each of the pollutants (for convenience Table 13 has been reproduced as Table B-2).

In the following paragraphs, the details of the analytical methods are presented separately for each class of pollutants, i.e., elemental, organic (PCB, POM) and minor anionic (sulfate, nitrate).

Table B-2. CHEMICAL ANALYSIS METHODS

Pollutant	Methods of analysis[a]
Trace elements (cations)	
Antimony	1[b]
Arsenic	1[b]
Barium	1
Beryllium	1
Cadmium	2
Chromium	1
Cobalt	1
Copper	1
Lead	2
Manganese	1
Mercury	2[c]
Nickel	1
Selenium	1[b]
Tellurium	1
Tin	2
Titanium	1
Vanadium	1
Zinc	1
Minor elements (cations)	
Calcium	1
Iron	1
Anions	
Chloride	3
Fluoride	4
Nitrate	7
Sulfate	8
Organics	
POM	6
PCB	5

---

[a] The methods of analysis are as follows:
- (1) Atomic Absorption Spectrometry (AAS), conventional flame methods;
- (2) AAS, micro flameless methods;
- (3) $AgNO_3$ titration, electrochemical (EC) detection;
- (4) EC, fluorine selective electrode;
- (5) Gas chromatography (GC), electron capture detection;
- (6) GC, flame ionization detection;
- (7) Spectrophotometric, phenol disulfonic acid complex; and
- (8) Barium perchlorate titration.

[b] AAS, hydride generation methods.

[c] AAS, cold vapor method.

Elemental Pollutants (cations)

Atomic absorption spectrophotometry (AAS) is the method of choice for the elements that commonly form cations. Some of the advantages of AAS are: the low limits of detection for most of the trace elements of interest; the large number of elements which can be analyzed; the low cost of highly reliable instrumentation; and, the accuracy and precision which can be obtained without highly trained technical personnel. Eleven of the 19 elements can be determined at the 10-ppm level with less than 1 g of sample. Conventional cold vapor and arsine generation techniques allow the determination of mercury and arsenic, respectively, at the 10-ppm level with less than 1 g of sample.

The recent development of micro methods using the carbon rod and tantalum strip atomizers enable analysis to be carried out on as little as 5 µl of solution, hence reducing the total volume of solution required to analyze 19 elements from > 25 ml to 1 to 5 ml. In addition, the solution detection limits are in the nanograms per milliliter rather than the micrograms per milliliter range of conventional flame methods. The low detection limit and low dilution factor make this technique the method of choice for the elemental pollutants that cannot be determined by conventional flame AAS because of insufficient sample size or sensitivity. The sensitivities of conventional and flameless methods are compared in Table B-3.

The minimum sample quantity required to accurately measure each elemental pollutant (relative standard deviation of 5 to 10%) by flameless AAS is given in Table B-4. In addition to required quantities of fly ash (for elements in the particulate state), the table also lists sample times for collection of sufficient amounts of vaporous elements.

The required quantities of fly ash were calculated with the following equation:

$$\text{Sample Required (mg)} = \frac{\text{Sensitivity (ng/ml)} \times 50 \times 5 \text{ ml}}{\text{Expected concentration } (\mu\text{g/g})}$$

where 50 = sensitivity multiplier which represents sufficient signal-to-noise ratio for a relative standard deviation of 5 to 10%

5 ml = volume of solution into which the sample is digested prior to analysis

Table B-3. ANALYSIS SENSITIVITY OF ATOMIC ABSORPTION SPECTROMETRY

Trace element (cation)	Sensitivity[a/] Conventional flame methods (μg/ml)	Flameless methods (ng/ml)
Antimony	0.6	6.0
Arsenic	1.3	0.1
Barium	0.3	
Beryllium	0.02	0.18
Cadmium	0.02	0.02
Chromium	0.09	1.0
Cobalt	0.09	1.2
Copper	0.04	1.4
Lead	0.16	1.0
Manganese	0.04	0.1
Mercury	2.0	20
Nickel	0.07	2.0
Selenium	0.6	20
Tellurium	0.3	
Thallium	0.26	
Tin	2.0	12
Titanium	2.2	
Vanadium	1.2	20
Zinc	0.012	0.02

---

a/ The concentration of a solution which produces a 1% absorption.

Table B-4. REQUIRED SAMPLE QUANTITIES FOR ANALYSIS OF ELEMENTAL POLLUTANTS BY FLAMELESS AAS

		Fly ash		Vapor[b]	
Trace element (cation)	Analysis sensitivity[a] (ng/ml)	Elemental concentration (μg/g)	Required sample quantity (mg)	Concentration in flue gases (mg/m^3)	Required sample time (min)
Antimony	6.0	50	30	0.33	8.66
Arsenic	0.1	320	0.078	2.1	0.022
Barium	300	500	150	-	-
Beryllium	0.18	24	1.9	-	-
Cadmium	0.02	0.3	17	-	-
Chromium	1.0	150	1.7	-	-
Cobalt	1.2	48	6.2	-	-
Copper	1.4	130	2.7	-	-
Lead	1.0	95	2.6	-	-
Manganese	0.1	500	0.050	-	-
Mercury	20	1.5	3,300	0.01	940
Nickel	2.0	150	3.3	-	-
Selenium	20	22	230[c]	0.15	63
Tellurium	20	10	500	-	-
Thallium	20	3	1,700	0.02	470
Tin	12	9.0	330[c]	-	-
Titanium	2,200	3,800	140	-	-
Vanadium	20	260	19	-	-
Zinc	0.02	120	0.042	-	-

---

a/ Sensitivity is defined as the concentration required to produce a 1% absorption.

b/ Data are given only for elements likely to be in vaporous form.[33]

c/ Approximately 10 mg of sample would allow analysis of these elements at a signal-to-noise level slightly greater than 2.

The concentration of an element in fly ash is calculated by multiplying the average concentration in coal (Table B-4) by 10.

Although the calculated minimum quantity of sample shown in Table B-4 is sometimes 5 mg or less, at least 10 mg and preferably 50 mg of each sample is desirable to reduce problems involved in sample handling and contamination.

The required time for collection of sufficient amounts of vaporous elements was calculated with the following equation:

$$\text{Time Required (min)} = \frac{\text{Sensitivity (ng/ml)} \times 50 \times 200 \text{ ml} \times K}{0.75 \text{ cfm} \times \text{Expected concentration (mg/m}^3\text{)}}$$

where 50 = sensitivity multiplier which represents sufficient signal-to-noise ratio for a relative standard deviation of 5 to 10%

200 ml = volume of impinger liquid which collected the sample

0.75 cfm = flue gas sampling rate

$$K = \frac{10^{-6} \text{ mg/ng}}{0.0283 \text{ m}^3/\text{ft}^3}$$

The concentration of vapor in the flue gases, assuming all the element is present in the vapor state, is calculated by dividing the average concentration in coal (Table B-4) by 15.*

Conventional flame AAS is used when sufficient sample quantities and detection limits can be obtained. Micro methods are more subject to contamination and may not include a representative portion of large (> 1 g) samples.

Interferences do occur in both conventional and micro AAS methods. To control chemical interferences, one must optimize instrumental parameters including selection of the proper flame mixture, temperature, and region. Chemical interferences due to matrix effects can enhance or depress absorption. These interferences can often be eliminated by adding releasing or chelating agents.

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* This factor is derived from the approximation that 200 ft^3 of flue gases at 300°F are produced by the combustion of 1 lb of coal.

Physical interferences, e.g., light scattering by particles in the atomization process, can be a source of error, especially in carbon rod atomization. Also, molecular absorption and emission can result in erroneous results if not corrected. Background correction techniques using nonabsorbing lines or hydrogen continuum lamps is applied for trace element analysis, especially when using flameless methods.

The sample preparation procedures for AAS depend upon the sample matrices. For this study, the types of matrices anticipated are whole coal, coal ash, and acid-permanganate solution. A suitable preparation for these matrices is the acid-pressure decomposition technique developed by Bernas.[40] This procedure has been applied to 12 of the 19 toxic pollutants of interest including refractory forming elements, e.g., Ba, Ti, and V. This procedure coupled with AAS has been applied to the analysis of granite, coal, coal ash, glass, and fish tissue for 18 elements and resulted in a relative standard deviation of approximately 5% for trace elements. The procedure has the following advantages: elimination of interelement and ionization interferences; elimination of volatilization and retention losses; relatively low cost per analysis because of the reduction in time and supervision required and the elimination of expensive platinum ware.

In this method, the samples are decomposed in a Teflon cup encapsuled in a stainless steel bomb with a decomposition medium of hydrofluoric and boric acid. The samples are digested for 0.5 to 3 hr at 110 to 170°C; the more rigorous conditions are applied to samples of higher organic content. Coal samples will be dry ashed prior to acid decomposition.

Two methods of sample preparation are used for the acid-permanganate solutions used to collect elements that might be present as vapors in the effluent gas stream. The first, is used for mercury determination by the cold vapor technique, includes digestion with fresh acid-permanganate followed by reduction with hydroxyl amine (for excess permanganate) and stannous chloride. The second portion of the acid-permanganate solutions is treated with sodium borohydride to form the hydrides of arsenic, selenium, and antimony prior to their determination by AAS using an argon-hydrogen entrained air flame.

Elemental Pollutants (anions)

Fluorine and chlorine cannot be determined by AAS. Samples are analyzed for fluorides following digestion under pressure in a sodium hydroxide medium. After buffering, fluorides are determined with a fluoride selective electrode. The practical limit of detection is 10 µg of fluoride per gram of sample. Chlorine is determined by igniting the samples in a bomb and titrating the aqueous washings with silver nitrate. The practical limit of detection is 0.01 to 0.03%.

Organic Pollutants

The organic compounds in the particulate matter can be separated from the total particulate by extraction with benzene. The separated organic material, the organic material collected in the Na_2CO_3 impingers and the Tenax-GC® plug are analyzed for POM and PCB.

POM Analysis - The POM in the benzene soluble fraction has been separated from PCB, aliphatic and heterocyclic compounds by column chromatography with activated silica gel as the adsorbent.[41]

Following the isolation of the total POM, gas chromatography with electron capture detection is used to quantify individual POM. Solution detection limits are in the 0.2 to 0.5 µg/ml range. Lao et al[29a] used a Dexsil-300 packed column to separate 70 POM. This packing has been used in our laboratory for benz[a]pyrene analysis and can be used to separate the 8 POM listed in Table 4. Quantification of 5 POM* will be made by comparing sample peak areas with areas obtained from synthetic mixtures. From Lao's work, benzo[c]phenanthrene and dibenzo[a,h]-pyrene can be identified by relative retention times. However, there is no information on GC analysis of dibenzo[a,g]carbazole or Dexsil-300, making identification impossible without a standard.

To verify the presence of POM, selected samples are analyzed by gas chromatography-mass spectrometry (GC-MS). At least 10 µg of a compound per milliliter of extract are required for identification of individual POM with a high degree of confidence by GC/MS.

PCB Analysis - PCB is determined by gas chromatography with electron capture detection. Solution detection limits are in the sub parts per million range. Other electron capturing materials can interfere with PCB analysis. The chromatographic method described by Armour and Burke[39] was used to separate and quantify the PCB in the benzene extract. The interfering electron capturing materials are eliminated by this method. Total PCB is determined by comparing total sample peak areas with the area obtained from a representative PCB standard.

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* Standards cannot be obtained for benzo[c]phenanthrene, dibenzo[a,h]-pyrene, and dibenzo[c,g]carbazole.

Sulfates and Nitrates

Water soluble sulfates and nitrates can be extracted with hot water and the extract divided into two portions. Sulfates are determined by microtitration with barium perchlorate using a Thorin indicator. Nitrates are determined spectrophotometrically after complexing with phenol disulfonic acid.

ALTERNATE ANALYSIS METHODS

This section contains a brief description of methods of analysis that meet the accuracy, precision, detection limit, and sample size requirements for the analysis of a number of pollutants pertinent to this study. In some cases, the methods listed below are equal to the method of choice listed in previous paragraphs, but have a higher cost per analysis or require more expensive instrumentation.

Neutron Activation Analysis (NAA)

The application of NAA to the elemental pollutants of interest has been shown to be feasible in coal and coal ash matrices. This technique has the advantage of being a sensitive multielement technique. Generally, the detection limits and accuracies obtained for these elements by NAA are comparable to those obtained by AAS. However, to achieve optimum sensitivity and to remove interfering radioactivity from other elements, chemical separations are usually required. The sample preparation techniques are usually specific for one or a few elements so that several methods would be required to improve the sensitivity and specificity for the 18 elements of interest.

The instrumentation required for NAA is sophisticated and expensive. Included in the basic instrumentation are an irradiation source, i.e., a nuclear reactor, a pulse height analyzer and a high resolution lithium-drifted germanium detector system.

Current work at Oak Ridge National Laboratory is directed toward the detection of elemental pollutants by nondestructive methods, i.e., without chemical treatment. Computer programs are being developed to identify X-ray photopeaks, assign and catalog energies, identify nuclides, etc. The goals are to eliminate separations, minimize interferences from high concentration components and reduce post-irradiation counting time. However, the state of the art for NAA analysis of the 18 elements of interest requires the most costly chemical separation techniques at the micrograms per gram.

X-Ray Fluorescence (XRF)

X-ray fluorescence is a multielement technique that can be applied to most of the elements of interest; the analysis of beryllium and boron by XRF is not feasible. The detection limits (50 to 1,000 ppm) without extensive preconcentration steps are generally 1 to 2 orders of magnitude higher than AAS and NAA. Conventional XRF techniques require sample sizes of 1 to 10 g.

X-ray fluorescence equipment is available for simultaneous determination of as many as 10 elements. The technique can be totally automated with a resulting low cost for routine analysis if the required sample size and element concentrations are available.

The combination of XRF with electron microprobe analysis does offer the unique capability of determining the size and elemental composition of particles. In this technique, a focused beam of electrons is moved across the surface of the sample to be examined. The electrons cause the emission of low energy secondary electrons. The images of the particles in the sample are depicted by these electrons. Resolutions of 200 Å (0.02 μ) can be obtained. The focused electron beam generates X-rays in addition to low energy electrons. Measurement of the X-rays results in the determination of the elements present. Particles as small as 0.5 μ can be analyzed at concentrations as low as one part per thousand.

Spark Source Mass Spectrometry (SSMS)

SSMS is best suited to survey an unknown sample for all possible elements including trace and major constituents. The detection limits are in the parts per billion range for all elements. The required sample size is from 10 to 100 mg. Detection of positively charged ions can be made photographically or electronically. The accuracy of SSMS when operated as a survey technique, i.e., when no standard is available, is within a factor of 10 of the correct answer. The accuracy can be improved to ± 30% if standard reference materials are available or by using synthetic standards if matrices can be adequately matched.

Isotope dilution is the most accurate SSMS technique. This technique can be applied to elements with two or more stable isotopes. The sample must be spiked with an isotope in the same chemical oxidation state. NBS results indicate that the isotope dilution technique can be applied to 10 of the 18 elemental pollutants at the 0.1 ppm level for 1-g samples. The dynamic range for a single isotope spike is limited to 30. This range limitation makes isotope dilution SSMS best suited for testing samples for compliance to preset standards.

Electrochemical Methods

Of the many electroanalytical methods available, anodic stripping voltametry appears to be the best suited for trace pollutant analysis. Electrochemical methods have the advantages of inexpensive instrumentation and minimum sample manipulation. However, they have narrower applicability than AAS and NAA. Of the elements listed in Table B-2, the stripping technique is especially suited for the analysis of Cd, Cu, Pb, and Zn; detection limits for these elements are in the sub parts per billion.

APPENDIX C

CALCULATION OF BOILER STEAM EFFICIENCY

This appendix outlines the procedures for calculating boiler steam efficiency using the abbreviated heat loss method specified in ASME Performance Test Code 4.1 (1964).

The efficiency of steam generating equipment determined within the scope of the ASME Code is the gross efficiency and is defined as the ratio of the heat absorbed by the working fluid to the heat input. This definition disregards the equivalent heat in the power required by the auxiliary apparatus external to the envelope (Figure C-1).

For conducting an abbreviated efficiency test that considers only the major losses and only the chemical heat in the fuel as input, the ASME data summary form and calculation form (Tables C-1 and C-2, respectively) are used. The mathematical scheme used to calculate boiler steam efficiency by the abbreviated heat loss method consists of the following 10 equations:

$$C_b = \frac{C}{100} - \frac{W_r \times H_r}{14{,}500} \qquad (1)$$

where C_b = pounds of carbon burned per pound of "as fired" fuel
C = percent carbon in "as fired" fuel (ultimate analysis)
W_r = pounds of dry refuse per pound of "as fired" fuel
H_r = heating value of total dry refuse (Btu/lb)

$$W_g = \frac{11\ CO_2 + 8\ O_2 + 7(N_2 + CO)}{3\ (CO_2 + CO)} \times \left[C_b + \frac{S}{2.67}\right] \qquad (2)$$

where W_g = pounds of dry gas per pound of "as fired" fuel
CO_2, O_2, N_2, CO = composition of dry flue gas (% by volume)
S = pounds sulfur per pound "as fired" fuel (ultimate analysis)
C_b = pounds of carbon burned per pound of "as fired" fuel

$$EA = 100 \times \left[\frac{O_2 - 0.5\ CO}{0.2682\ N_2 - O_2 + 0.5\ CO}\right] \qquad (3)$$

where EA = excess air (%)
O_2, CO, N_2 = composition of dry flue gas (% by volume)

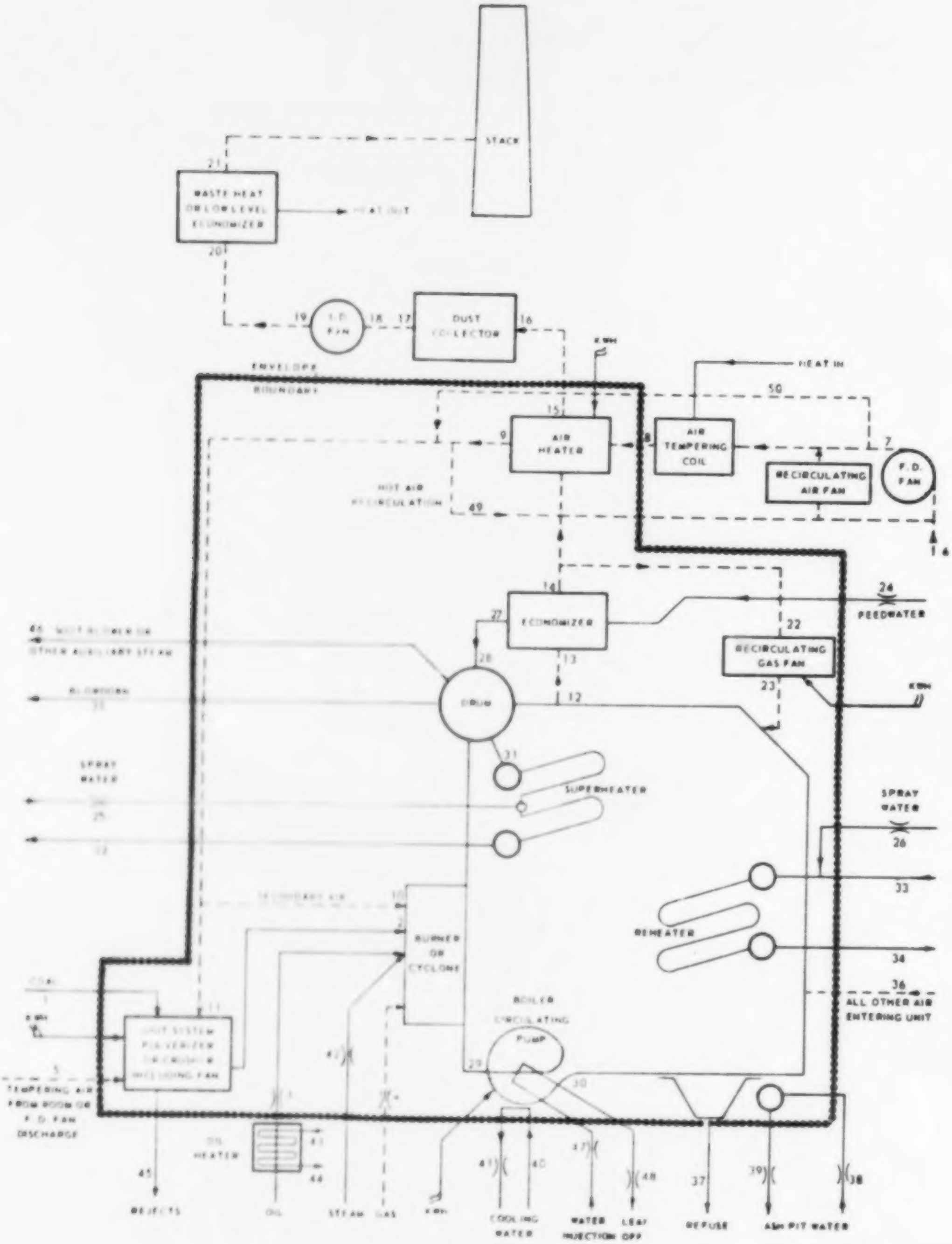
STACK
21
WASTE HEAT OR LOW LEVEL ECONOMIZER
HEAT OUT
20
19
I.D. FAN
18
17
DUST COLLECTOR
16
KWH
ENVELOPE BOUNDARY
HEAT IN
50
15
9
AIR HEATER
8
AIR TEMPERING COIL
7
RECIRCULATING AIR FAN
F.D. FAN
HOT AIR RECIRCULATION
49
6
14
27
ECONOMIZER
24
FEEDWATER
22
RECIRCULATING GAS FAN
28
13
23
KWH
46 SOOT BLOWER OR OTHER AUXILIARY STEAM
BLOWDOWN
35
DRUM
12
31
SPRAY WATER
25
SUPERHEATER
32
SPRAY WATER
26
33
SECONDARY AIR
10
2
BURNER OR CYCLONE
REHEATER
34
36
ALL OTHER AIR ENTERING UNIT
COAL
1
KWH
11
UNIT SYSTEM PULVERIZER OR CRUSHER INCLUDING FAN
BOILER CIRCULATING PUMP
5
TEMPERING AIR FROM ROOM OR F.D. FAN DISCHARGE
42
29
30
3
4
OIL HEATER
43
44
41
40
47
48
37
39
38
45
REJECTS
OIL
STEAM
GAS
KWH
COOLING WATER
WATER INJECTION
LEAK OFF
REFUSE
ASH PIT WATER

Figure C-1. Steam generating unit diagram.

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SUMMARY SHEET

ASME TEST FORM
FOR ABBREVIATED EFFICIENCY TEST

PTC 4.1-a (1964)

TEST NO BOILER NO DATE
OWNER OF PLANT LOCATION
TEST CONDUCTED BY OBJECTIVE OF TEST DURATION
BOILER MAKE & TYPE RATED CAPACITY
STOKER TYPE & SIZE
PULVERIZER TYPE & SIZE BURNER, TYPE & SIZE
FUEL USED MINE COUNTY STATE SIZE AS FIRED

PRESSURES & TEMPERATURES

1	STEAM PRESSURE IN BOILER DRUM	psia	
2	STEAM PRESSURE AT S. H. OUTLET	psia	
3	STEAM PRESSURE AT R. H. INLET	psia	
4	STEAM PRESSURE AT R. H. OUTLET	psia	
5	STEAM TEMPERATURE AT S. H. OUTLET	F	
6	STEAM TEMPERATURE AT R. H. INLET	F	
7	STEAM TEMPERATURE AT R. H. OUTLET	F	
8	WATER TEMP. ENTERING (ECON.)(BOILER)	F	
9	STEAM QUALITY% MOISTURE OR P. P. M.		
10	AIR TEMP. AROUND BOILER (AMBIENT)	F	
11	TEMP AIR FOR COMBUSTION (This is Reference Temperature) †	F	
12	TEMPERATURE OF FUEL	F	
13	GAS TEMP. LEAVING (Boiler) (Econ.) (Air Htr.)	F	
14	GAS TEMP. ENTERING AH (If conditions to be corrected to guarantee)	F	

UNIT QUANTITIES

15	ENTHALPY OF SAT. LIQUID (TOTAL HEAT)	Btu/lb	
16	ENTHALPY OF (SATURATED)(SUPERHEATED) STM	Btu/lb	
17	ENTHALPY OF SAT. FEED TO (BOILER) (ECON.)	Btu/lb	
18	ENTHALPY OF REHEATED STEAM R.H. INLET	Btu/lb	
19	ENTHALPY OF REHEATED STEAM R. H. OUTLET	Btu/lb	
20	HEAT ABS/LB OF STEAM (ITEM 16 – ITEM 17)	Btu/lb	
21	HEAT ABS/LB R.H. STEAM (ITEM 19 – ITEM 18)	Btu/lb	
22	DRY REFUSE (ASH PIT + FLY ASH) PER LB AS FIRED FUEL	lb/lb	
23	Btu PER LB IN REFUSE (WEIGHTED AVERAGE)	Btu/lb	
24	CARBON BURNED PER LB AS FIRED FUEL	lb/lb	
25	DRY GAS PER LB AS FIRED FUEL BURNED	lb/lb	

HOURLY QUANTITIES

26	ACTUAL WATER EVAPORATED	lb/hr	
27	REHEAT STEAM FLOW	lb/hr	
28	RATE OF FUEL FIRING (AS FIRED wt)	lb/hr	
29	TOTAL HEAT INPUT $\frac{\text{Item 28} \times \text{Item 41}}{1000}$	kB/hr	
30	HEAT OUTPUT IN BLOW-DOWN WATER	kB/hr	
31	TOTAL HEAT OUTPUT $\frac{(\text{Item 26} \times \text{Item 20}) + (\text{Item 27} \times \text{Item 21}) + \text{Item 30}}{1000}$	kB/hr	

FLUE GAS ANAL. (BOILER)(ECON)(AIR HTR) OUTLET

32	CO_2	% VOL	
33	O_2	% VOL	
34	CO	% VOL	
35	N_2 (BY DIFFERENCE)	% VOL	
36	EXCESS AIR	%	

FUEL DATA

COAL AS FIRED PROX. ANALYSIS		% wt
37	MOISTURE	
38	VOL MATTER	
39	FIXED CARBON	
40	ASH	
	TOTAL	
41	Btu per lb AS FIRED	
42	ASH SOFT TEMP.* ASTM METHOD	

OIL		
51	FLASH POINT F*	
52	Sp. Gravity Deg. API*	
53	VISCOSITY AT SSU* BURNER SSF	
44	TOTAL HYDROGEN % wt	
41	Btu per lb	

COAL OR OIL AS FIRED ULTIMATE ANALYSIS		
43	CARBON	
44	HYDROGEN	
45	OXYGEN	
46	NITROGEN	
47	SULPHUR	
40	ASH	
37	MOISTURE	
	TOTAL	

	GAS	% VOL
54	CO	
55	CH_4 METHANE	
56	C_2H_2 ACETYLENE	
57	C_2H_4 ETHYLENE	
58	C_2H_6 ETHANE	
59	H_2S	
60	CO_2	
61	H_2 HYDROGEN	
	TOTAL	
	TOTAL HYDROGEN % wt	
62	DENSITY 68 F ATM. PRESS.	
63	Btu PER CU FT	
41	Btu PER LB	

COAL PULVERIZATION		
48	GRINDABILITY INDEX*	
49	FINENESS % THRU 50 M*	
50	FINENESS % THRU 200 M*	

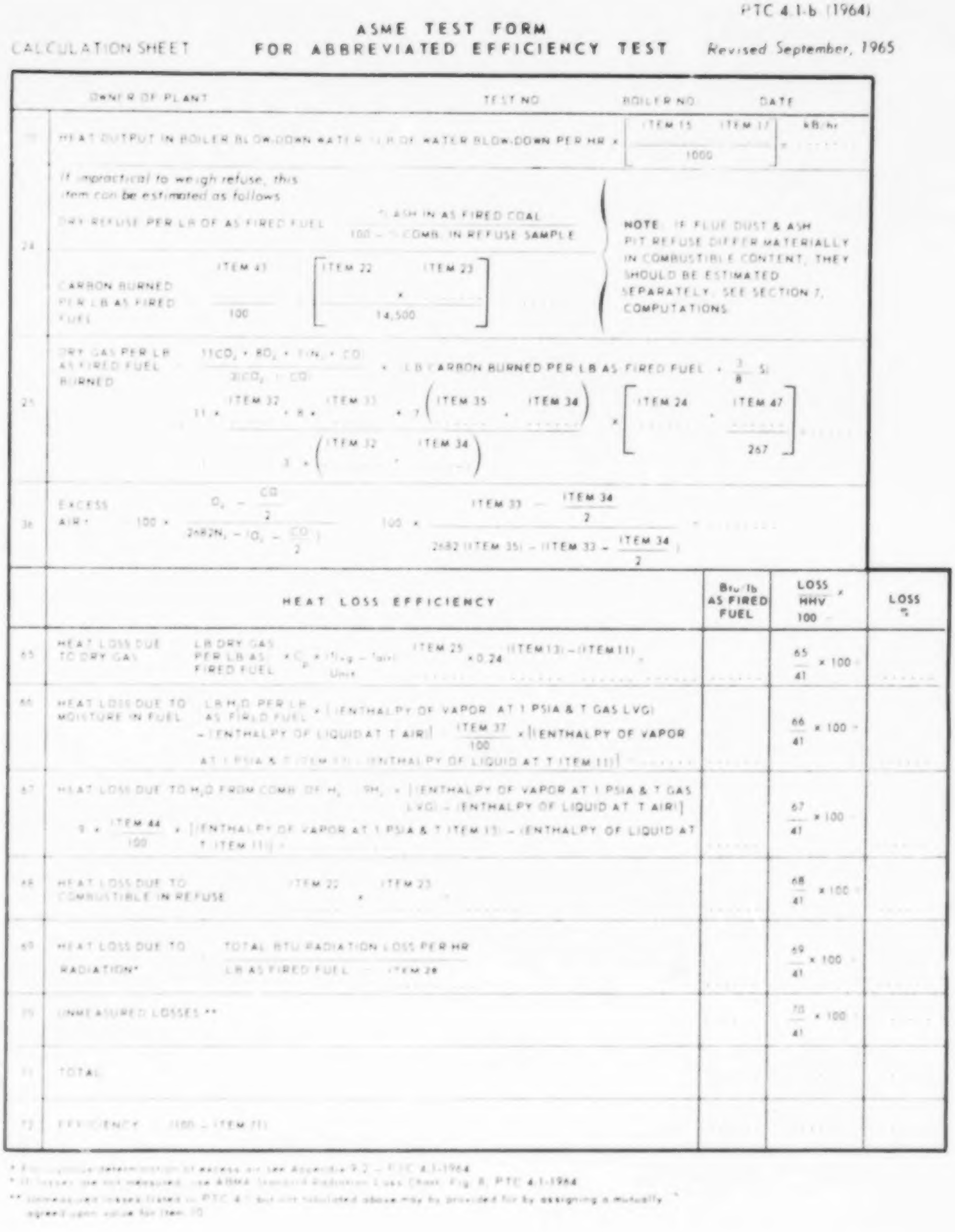
64	INPUT-OUTPUT EFFICIENCY OF UNIT %	$\frac{\text{ITEM 31} \times 100}{\text{ITEM 29}}$

	HEAT LOSS EFFICIENCY	Btu/lb A. F. FUEL	% of A. F. FUEL
65	HEAT LOSS DUE TO DRY GAS		
66	HEAT LOSS DUE TO MOISTURE IN FUEL		
67	HEAT LOSS DUE TO H_2O FROM COMB. OF H_2		
68	HEAT LOSS DUE TO COMBUST. IN REFUSE		
69	HEAT LOSS DUE TO RADIATION		
70	UNMEASURED LOSSES		
71	TOTAL		
72	EFFICIENCY = (100 – Item 71)		

* Not Required for Efficiency Testing

† For Point of Measurement See Par. 7.2.8.1-PTC 4.1-1964

Table C-1



PTC 4.1-b (1964)

CALCULATION SHEET — **ASME TEST FORM FOR ABBREVIATED EFFICIENCY TEST** — *Revised September, 1965*

OWNER OF PLANT — TEST NO. — BOILER NO. — DATE

19 HEAT OUTPUT IN BOILER BLOW-DOWN WATER = LB OF WATER BLOW-DOWN PER HR × $\left[\dfrac{\text{ITEM 15} - \text{ITEM 17}}{1000}\right]$ = kB/hr

24 *If impractical to weigh refuse, this item can be estimated as follows*

DRY REFUSE PER LB OF AS FIRED FUEL = $\dfrac{\text{\% ASH IN AS FIRED COAL}}{100 - \text{\% COMB. IN REFUSE SAMPLE}}$

CARBON BURNED PER LB AS FIRED FUEL = $\dfrac{\text{ITEM 43}}{100} - \left[\dfrac{\text{ITEM 22} \times \text{ITEM 23}}{14{,}500}\right]$ =

NOTE: IF FLUE DUST & ASH PIT REFUSE DIFFER MATERIALLY IN COMBUSTIBLE CONTENT, THEY SHOULD BE ESTIMATED SEPARATELY. SEE SECTION 7, COMPUTATIONS.

25 DRY GAS PER LB AS FIRED FUEL BURNED = $\dfrac{11CO_2 + 8O_2 + 7(N_2 + CO)}{3(CO_2 + CO)} \times \left(\text{LB CARBON BURNED PER LB AS FIRED FUEL} + \dfrac{3}{8}S\right)$

$$= \frac{11 \times \text{ITEM 32} + 8 \times \text{ITEM 33} + 7(\text{ITEM 35} + \text{ITEM 34})}{3 \times (\text{ITEM 32} + \text{ITEM 34})} \times \left[\text{ITEM 24} + \frac{\text{ITEM 47}}{267}\right] =$$

36 EXCESS AIR† = $100 \times \dfrac{O_2 - \dfrac{CO}{2}}{.2682N_2 - (O_2 - \dfrac{CO}{2})} = 100 \times \dfrac{\text{ITEM 33} - \dfrac{\text{ITEM 34}}{2}}{.2682(\text{ITEM 35}) - (\text{ITEM 33} - \dfrac{\text{ITEM 34}}{2})}$ =

	HEAT LOSS EFFICIENCY	Btu/lb AS FIRED FUEL	LOSS/HHV × 100 =	LOSS %
65	HEAT LOSS DUE TO DRY GAS = LB DRY GAS PER LB AS FIRED FUEL × C_p × $(t_{lvg} - t_{air})$ = ITEM 25 × 0.24 (ITEM 13) − (ITEM 11) =		$\frac{65}{41}$ × 100 =	
66	HEAT LOSS DUE TO MOISTURE IN FUEL = LB H_2O PER LB AS FIRED FUEL × [(ENTHALPY OF VAPOR AT 1 PSIA & T GAS LVG) − (ENTHALPY OF LIQUID AT T AIR)] = $\frac{\text{ITEM 37}}{100}$ × [(ENTHALPY OF VAPOR AT 1 PSIA & T ITEM 13) − (ENTHALPY OF LIQUID AT T ITEM 11)] =		$\frac{66}{41}$ × 100 =	
67	HEAT LOSS DUE TO H_2O FROM COMB. OF H_2 = $9H_2$ × [(ENTHALPY OF VAPOR AT 1 PSIA & T GAS LVG) − (ENTHALPY OF LIQUID AT T AIR)] = 9 × $\frac{\text{ITEM 44}}{100}$ × [(ENTHALPY OF VAPOR AT 1 PSIA & T ITEM 13) − (ENTHALPY OF LIQUID AT T ITEM 11)] =		$\frac{67}{41}$ × 100 =	
68	HEAT LOSS DUE TO COMBUSTIBLE IN REFUSE = ITEM 22 × ITEM 23 =		$\frac{68}{41}$ × 100 =	
69	HEAT LOSS DUE TO RADIATION* = $\frac{\text{TOTAL BTU RADIATION LOSS PER HR}}{\text{LB AS FIRED FUEL} - \text{ITEM 28}}$		$\frac{69}{41}$ × 100 =	
70	UNMEASURED LOSSES **		$\frac{70}{41}$ × 100 =	
71	TOTAL			
72	EFFICIENCY = (100 − ITEM 71)			

† For rigorous determination of excess air see Appendix 9.2 — PTC 4.1-1964

* If losses are not measured, use ABMA Standard Radiation Loss Chart, Fig. 8, PTC 4.1-1964

** Unmeasured losses listed in PTC 4.1 but not tabulated above may by provided for by assigning a mutually agreed upon value for Item 70.

Table C-2

$$L_g = W_g \times c_p \times (t_1 - t_a) \qquad (4)$$

where L_g = heat loss due to heat in dry flue gas (Btu/lb of "as fired" fuel)
W_g = pounds of dry gas per pound of "as fired" fuel
c_p = mean specific heat of dry flue gas = 0.24 Btu/lb °F
t_1 = temperature of gas leaving boiler (°F)
t_a = reference temperature of air for combustion (°F)

$$L_{m_f} = m_f \times (h_{t_1} - h_{t_a}) \qquad (5)$$

where L_{m_f} = heat loss due to moisture in "as fired" fuel
m_f = pounds of water per pound of "as fired" fuel
h_{t_1} = enthalpy of vapor at 1 psia and t_1
h_{t_a} = enthalpy of vapor at 1 psia and t_a

$$L_H = 9\ H_2 \times (h_{t_1} - h_{t_a}) \qquad (6)$$

where L_H = heat loss due to moisture from combustion of hydrogen (Btu/lb of "as fired" fuel)
H_2 = pounds of hydrogen per pound of "as fired" fuel (ultimate analysis)
h_{t_1} and h_{t_a} = as defined in Eq. (5)

$$L_{UC} = W_r \times H_r \qquad (7)$$

where L_{UC} = heat loss due to unburned carbon (Btu/lb of "as fired" fuel)
W_r and H_r = as defined in Eq. (1)

$$L_R = \frac{R_p}{100} \times HHV \qquad (8)$$

where L_R = heat loss due to radiation (Btu/lb)
R_p = radiation loss as percent of gross heat input
HHV = heat of combustion (Btu/lb from proximate analysis)

$$L = L_g + L_{m_f} + L_H + L_{UC} + L_R \qquad (9)$$

where L = total heat loss (Btu/lb)
L_g = heat loss due to heat in dry gas (Eq. (4))
L_{m_f} = heat loss due to moisture in fuel (Eq. (5))
L_H = heat loss due to H_2O from combustion of H_2 (Eq. (6))
L_{UC} = heat loss due to unburned carbon (Eq. (7))
L_R = heat loss due to radiation (Eq. (8))
All above in units of Btu/lb

$$\eta_g = 100 - \frac{L}{HHV} \times 100 \qquad (10)$$

where η_g = gross efficiency (%)
L = total heat loss (Eq. (9))
HHV = as defined in Eq. (8)

Application of the heat loss method to the data from Widows Creek Run 4 yields the following:

$$C_b = \frac{63.75}{100} - \left[\frac{0.197 \times 300}{14{,}500}\right] = 0.6334 \text{ lb C/lb fuel} \qquad (1)$$

$$W_g = \frac{11\ (12.7) + 8\ (5.8) + 7\ (81.2 + 0.3)}{3\ (12.7 + 0.3)} \times 0.6334 + \frac{0.0395}{2.67}$$

$$= 12.6 \text{ lb dry gas/lb fuel} \qquad (2)$$

$$EA = 100 \times \left[\frac{5.8 - 0.5\ (0.3)}{0.2682\ (81.2) - 5.8 + 0.5\ (0.3)}\right] = 35.0\% \qquad (3)$$

$$L_g = 12.6 \times 0.24 \times (360 - 100) = 786 \text{ Btu/lb} \qquad (4)$$

$$L_{m_f} = 0.0138 \times (1{,}222.7 - 67.9) = 15.9 \text{ Btu/lb} \qquad (5)$$

$$L_H = 9\ (0.0447) \times (1{,}222.7 - 67.9) = 465 \text{ Btu/lb} \qquad (6)$$

$$L_{UC} = 0.197 \times 300 = 59.1 \text{ Btu/lb} \qquad (7)$$

$$L_R = \frac{0.44}{100} \times 11{,}541 = 50.8 \text{ Btu/lb} \qquad (8)$$

$$L = 786 + 15.9 + 465 + 59.1 + 50.8 = 1{,}377 \text{ Btu/lb} \qquad (9)$$

$$\eta_g = 100 - \left[\frac{1{,}377}{11{,}541}\right] \times 100 \quad = 88.1\% \qquad (10)$$

Note that in estimating the value of 0.44 for the radiation loss as percent of gross heat input (Eq. (8)), the following assumptions were made:

1. One megawatt of generating capacity is equivalent to 10^7 Btu/hr of heat output.

2. The temperature differential between the outer furnace wall and the surrounding air was 100° F.

The calculated value of 88.1% for the boiler steam efficiency is very close to the design value of 88.45%.

APPENDIX D

CALCULATION PROCEDURE FOR MASS BALANCE PRECISION

1. Introduction

Table D-1 defines the variances in the mass balances calculated in Section VIII of this report. The following subsections of this appendix document (a) the general statistical equations used in the calculations and (b) the methodology for calculation of $V(M)_T$, $V(M)_A$, $V(M)_P$, and $V(M)_S$, respectively. ($V(M)_A$, $V(M)_P$, and $V(M)_S$ are component parts which totalled together equal $V(M)_T$.)

Table D-1. DEFINITIONS OF VARIANCES

$V(M)_T$	The total variance in the actual mass imbalance which includes: (1) analytical variability, $V(M)_A$, (2) process variability, $V(M)_P$, and (3) variance due to nonrepresentative sampling, $V(M)_S$.
$V(M)_A$	The theoretical variability in the mass imbalance if errors arose only from imprecision of the laboratory analysis results.
$V(M)_P$	The theoretical variability in the mass imbalance if errors arose only from run to run changes in pollutant concentration.
$V(M)_S$	The difference between the total variability in the mass imbalance, $V(M)_T$, and the sum of $V(M)_A$ and $V(M)_P$. Ideally, this "sampling" error represents the "errors of the sample," i.e., the inaccuracy of the result arising from the fact that only a finite number of samples were examined (as opposed to the whole population). We have no direct way of estimating this, however, since we took only a sample size of 1 under each condition.

2. General Equations

Consider the basic equation for calculation of fractional mass imbalance:

$$M = \frac{\text{Output - Input}}{\text{Input}} \qquad (1)$$

Let c_i be the concentration (ppm) in each stream i , where:

i	Stream	Stream abbreviation
1	Coal	C
2	Bottom ash	BA
3	Superheater ash	SA
4	Dust collector ash	DCA
5	Outlet fly ash	OFA

Let w_i be the flow rate through each corresponding stream i .

The fractional mass imbalance can then be considered as:

$$M = \frac{w_2c_2 + w_3c_3 + w_4c_4 + w_5c_5 - w_1c_1}{w_1c_1} \tag{2}$$

or $$M = \left(\frac{w_2}{w_1}\right)\left(\frac{c_2}{c_1}\right) + \left(\frac{w_3}{w_1}\right)\left(\frac{c_3}{c_1}\right) + \left(\frac{w_4}{w_1}\right)\left(\frac{c_4}{c_1}\right) + \left(\frac{w_5}{w_1}\right)\left(\frac{c_5}{c_1}\right) - 1 \tag{3}$$

Let $y_k = \frac{w_{k+1}}{w_1}$ and $x_k = \frac{c_{k+1}}{c_1}$ (4 and 5)

Thus, $M = y_1x_1 + y_2x_2 + y_3x_3 + y_4x_4 - 1$ (6)

Then, letting $z_k = y_kx_k$:

$$M = z_1 + z_2 + z_3 + z_4 - 1 \tag{7}$$

The following general equations were used in the calculation of variances $V(M)_P$ and $V(M)_A$ for sums, products, and quotients, respectively:

$$V(M) = V(z_1) + V(z_2) + V(z_3) + V(z_4) \tag{8}$$

with:

$$V(z_i) = [\bar{x}_i^2 \; V(y_i) + \bar{y}_i \; V(x_i)]/N$$

where n = 3 based on the varying numbers of streams and sample size.

$$V(y_i) = \frac{V(w_{i+1}) + \bar{y}_i^2 \; V(w_1) - 2\bar{y}_i \; \mathrm{cov}(w_1 w_{i+1})}{n\bar{c}_1^2} , \tag{10}$$

where n = number of runs (= 2)

Redefining Eq. (10) in terms of x_i and c_i,

$$V(x_i) = \frac{V(c_{i+1}) + \bar{x}_i^2 \; V(c_1) - 2\bar{x}_i \; \mathrm{cov} \; (c_1 c_{i+1})}{n\bar{c}_1^2} \tag{11}$$

where the covariance, cov, is defined as:

$$\mathrm{cov}(w_1 w_{i+1}) = \frac{n \sum w_1 w_{i+1} - (\sum w_1) \; (\sum w_{i+1})}{n \; (n - 1)} \tag{12}$$

and

$$\mathrm{cov}(c_1 c_{i+1}) = \frac{n \sum c_1 c_{i+1} - (\sum c_1) \; (\sum c_{i+1})}{n \; (n - 1)} \tag{13}$$

3. Calculation Methodology

a. $V(M)_T$

The total variance in the actual mass imbalance, $V(M)_T$, can be calculated as follows:

$$V(M)_T = \frac{3 \; (m_2^2 + m_3^2 + m_4^2) - (m_2 + m_3 + m_4)^2}{6} \tag{14}$$

where m_2 , m_3 , and m_4 are the fractional mass imbalances as determined for each run (Runs Nos. 2, 3, and 4, respectively).

b. $\underline{V(M)_A}$

$V(M)_A$ represents the theoretical variability in the mass imbalance if errors arose only from imprecision of the laboratory results.

Duplicate samples for Runs Nos. 3 and 4 were analyzed by the same procedures. Since "within run" variation is considered here, variances between the duplicate samples were determined for each stream of Run No. 3 and each stream of Run No. 4, by the formula:

$$V(c_{ij}) = \frac{n\sum c_{ij}^2 - (\sum c_{ij})^2}{n\,(n - 1)} \tag{15}$$

where $n = 2$ (duplicate samples) and

i = stream number, 1 through 5

j = run number, 3 through 4

The average variance for each stream is:

$$V(c_i) = \frac{V(c_{i3}) + V(c_{i4})}{2} \tag{16}$$

By substitution of appropriate values into Eqs. (8) through (13) (in reverse order), Eq. (8) yields the result of $V(M)_A$ for each pollutant.

c. $\underline{V(M)_P}$

The calculation procedure for $V(M)_P$ parallels the procedure for calculation of $V(M)_A$. However, $V(M)_P$ is defined as the theoretical variability in the mass imbalance if errors arose only from run to run changes in pollutant concentration.

Instead of determining variances and covariances for each run and stream, and then averaging for each stream, as we did for calculation of $V(M)_A$, we considered the average values determined for Run No. 3 for each stream and the average values determined for Run No. 4 for each stream. The variance for each stream, between runs, can be calculated by:

$$V(c_i) = \frac{n\,(\sum c_i^2) - (\sum c_i)^2}{n\,(n-1)}$$

where n = 2 and the c_i's are summed for Runs Nos. 3 and 4.

Again, by substitution of the appropriate values into Eqs. (8) through (13) (in reverse order), Eq. (8) yields the result of $V'(M)_P$ for each pollutant. To obtain a measure of run to run changes in pollutant concentration, we subtracted out the analytical contribution. Thus,

$$V(M)_P = V'(M)_P - V(M)_A$$

d. $\underline{V(M)_S}$

$V(M)_S$ represents the "sampling" error or errors due to the fact that only a finite number of samples were taken (as opposed to the whole population).*

The formula used is as follows:

$$V(M)_S = V(M)_T - V(M)_A - V(M)_P$$

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* In Section IX, we defined nonrepresentative sampling as $V(M)_S$ + $V(M)_P$.

APPENDIX E

FACTORS FOR CONVERSION TO METRIC UNITS

English unit	Metric equivalent	Conversion factor (or equation)
barrels (oil)	m^3	0.1589873
Btu	joule	1055.056
Btu/hr	watt	0.2930711
Btu/kw-hr	watt/kw	0.2930711
Btu/lb	joule/kg	2326.012
cfm	m^3/min	0.028317
cu ft	m^3	0.028317
dscfm	nm^3/min	0.028317
dscfm/mw	nm^3/mw	0.028317
°F	°C	5/9 (°F - 32)
ft	m	0.3048
gr	g	0.064799
gr/10^6 Btu	g/10^6 joule	0.0009478
gr/acf	mg/m^3	2288.34
gr/scf	mg/nm^3	2288.34
horsepower	watt	745.6999
in.	cm	2.54
in. Hg	mm. Hg	25.4
lb	gm	453.59
lb/hr	kg/min	0.007558
miles	km	1.609344
ppm by volume	$\mu\ell/\ell$	1
ppm by weight	μg/gm	1
tons (short)	kg	907.1847
tons/hr	kg/hr	907.1847

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